Poster A1

COMPUTATIONAL STUDY OF CHARGED ELECTRODE INTERFACE IN IONIC LIQUIDS

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Due to wide electrochemical window and low vapor pressure ionic liquids seem to be a promising replacement for common electrolytes in energy storage systems. However, behavior of ILs dramatically differs from that of electrolyte solutions even concentrated ones. In this work a structure of the charged electrode interface (i.e. electrical double layer) in imidazolium-based ionic liquids is studied by means of molecular dynamic simulations. The electrical potential (Figure 2) and element density profiles are presented as well as its dependence on the surface charge and the choice of anion. The specific purpose is to predict chemical shifts of photoelectron spectra to interpret experimental XPS data.

The work was supported by Centre for Electrochemical Energy of Skolkovo Institute of Science and Technology.

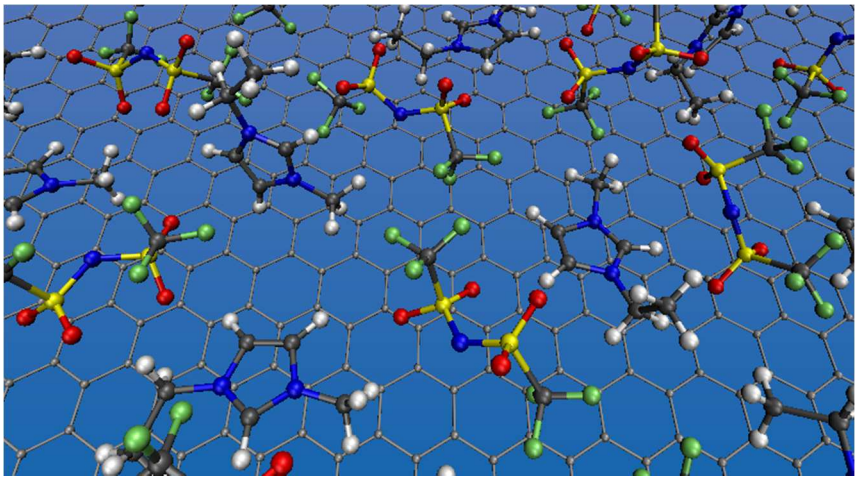

Figure 1. First monolayer of EMI-TFSI

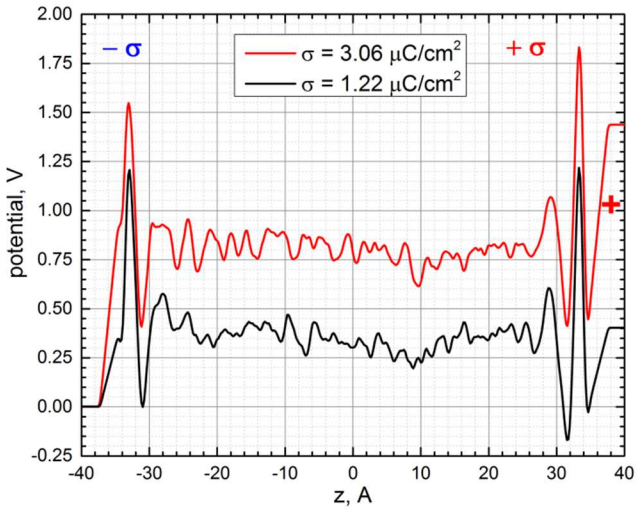

Figure 2. Potential profiles near charged surfaces in EMI-TFSI

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Poster A2

FIRST-PRINCIPLES CALCULATION OF PLASMONIC RESONANCES AND ELECTRIC FIELD ENHANCEMENT IN METAL-CLUSTER DIMERS

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Recent progress in fabrication of nanodevices has made possible the production of nanoobjects of controlled composition and shape down to atomic precision. Metallic clusters of Ag, Cu, Au have been used to amplify Raman spectroscopy signal [1]. One of the mechanism that leads to amplification of Raman signal is the enhancement of the electromagnetic field in the nanoscale [2]. Namely, if a metal cluster locates in the vicinity of a molecule, then the electromagnetic field induced by the cluster response can be much larger than the driving laser field.

In this work, we present an *ab-initio* study of the polarizability and electric field enhancement in the vicinity of metal cluster dimers. The approach is based on time-dependent density functional theory (TDDFT) because only TDDFT offers a feasible quantum-mechanical description for systems of several hundred of atoms. TDDFT reproduces the basic features of experimental absorption spectra and it allows to examine the spatial- and frequency-dependence of the field enhancement in nano-cavities of different sizes and shapes [3].

For our calculations, we employ an original implementation of TDDFT in the linear response regime [4]. This implementation is optimized for utilizing locality of operators in order to construct an algorithm of low computational complexity. Our TDDFT code is interfaced with SIESTA: an efficient density functional theory implementation [5]. The low complexity algorithms employed in SIESTA and in our TDDFT code made possible to address electric field enhancement between sodium cluster dimers composed of several hundreds of atoms. We perform a detailed analysis of the density change and the induced electric field distribution. From the calculations, we demonstrate that the atomic structure plays a crucial role for the absorption cross-section and the electric field enhancement, especially for small dimer separations. In the Figure 1, we show the electric field enhancement and the polarizability for a $2xNa_{380}$ dimer.

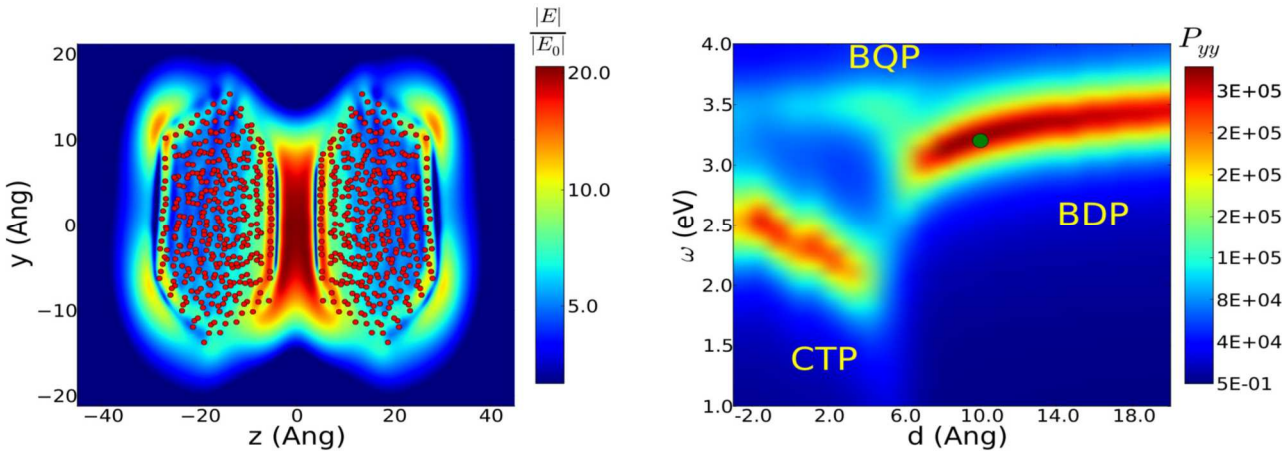

Figure 1. Left panel shows the electric field enhancement for the face to face geometry of Na_{380} dimers. Right panel shows the corresponding contour plot of the polarizability as function of separation distance d and frequency. The green dot marks parameters at which the electric field enhancement is plotted on the right panel.

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Poster A3

EFFECT OF DISORDER ON CHARGE TRANSPORT IN AN AMORPHOUS TRIPHENYLAMINE-FLUORENE COPOLYMER

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The alternate copolymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4-(N-(4-sec-butylphenyl)) diphenylamine, also known as TFB, is an amorphous system with relatively high hole mobility, which is widely used as a hole transporting and electron blocking polymer layer in organic optoelectronic devices [1,2]. It could be also considered as a model system for fundamental theoretical studies [3] due to its good semiconducting properties.

In the present work, a customized united-atom force field is adapted to model bulk TFB pentamers and molecular dynamics simulations are employed to generate corresponding morphologies for four different samples of TFB. Due to the relatively large size of the pentamers, the transfer integrals between oligomer orbitals and the HOMO levels is calculated at the Intermediate Neglect of Differential Overlap (INDO) semi-empirical level of theory [6] with the Coulomb repulsion term described by the Mataga-Nishimoto potential [7]. The value of transfer integral is thus defined by the overlap between the involved atomic orbitals [8]. A Kinetic Monte Carlo (KMC) scheme [9] is then employed by incorporating the evaluated charge transport parameters (electronic couplings, energy levels, and reorganization energy) so as to extract the charge carrier mobilities at different temperatures. Miller-Abrahams and Marcus kinetic models are employed in the KMC scheme for all four samples, and temperature and field dependence of the mobility are analyzed. Current work is aimed at addressing the effect of diagonal & off-diagonal disorders towards electric-field dependent behavior of charge transport.

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Poster A4

TOWARDS A METHOD FOR ASSESSING INTERFACIAL CHARGE TRANSFER PROCESSES IN FUTURE ENERGY DEVICES

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Organic photovoltaic devices are promising candidates for future, inexpensive, easy-to manufacture, and environmentally friendly energy devices. Nonetheless, a thorough understanding of interfacial charge transfer processes during their operation is still lacking. We investigate such processes by employing Green's functions techniques on top of semi-local density functional theory (DFT) calculations to assess the elastic lifetimes of electronic states localized on adsorbates, explicitly including the effect of the coupling to the semi-infinite substrate [1]. In order to test the performance of our computational technique [2] we have first analyzed simple, well-defined systems for which reliable experimental information exists. One interesting case, worth being studied, is core-excited Ar on Co(001) and Fe(110). For these systems recent core-hole-clock measurements [3] of the lifetime of the photo-excited 4s level of Ar* have shown a clear dependence on the spin of the excited electron. Minority electrons in the Ar* 4s state decay significantly faster than majority electrons. Our calculations agree with the observed behavior and allow analyzing in detail the origin of this phenomenon. In order to gain a better understanding we have performed a detailed analysis of the energy dependent substrate-adsorbate coupling. We have also considered different descriptions of the inherently ill-defined wave-packet describing the initial state of the photo-excited electron.

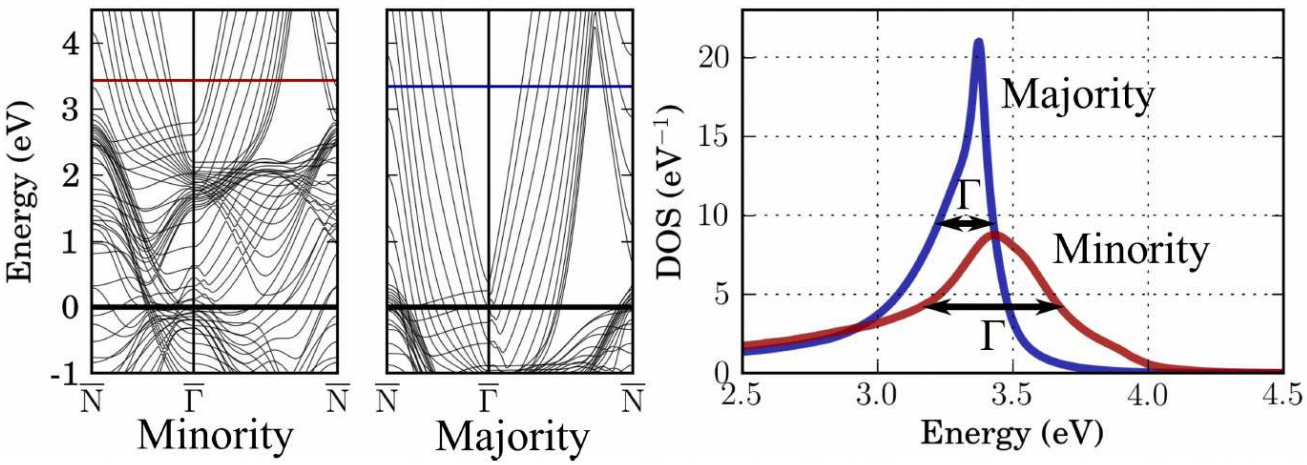

Figure 1. Left panels: Band structures for both spin projections of the Fe(110) surface and energetic positions of the corresponding calculated resonances (thin horizontal lines). A projected band gap is visible around the Γ-point at the resonances. Right panel: PDOS plots related to both spin projections for the extraction of the width Γ of the 4s state in order to receive an estimation of the corresponding lifetimes.

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Poster A5

EXPLOITING UNIQUE PROPERTIES OF LAYERED INORGANIC SEMICONDUCTORS

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In recent years, led by graphene, there has been an increased interest in 2D materials because of their unique properties. Certain transition metal oxides and chalcogenides (TMO&C) represent a class of these 2D materials forming layers that are held together by 'weak' interactions. Monolayers of these materials have been reported to have unique electronic properties (such as edge states [1]) in comparison to the traditional 3D lattice based semiconductors. Many of these TMO&Cs also exhibit thickness-dependent electronic properties which themselves are a focus of contemporary research [2]. In this work, we present our attempts at simulating the structural and electronic properties of a few TMO&Cs using density functional theory. We highlight the importance of accounting van der Waals interactions [3] to attain good agreement with experimental findings of structural parameters. We also outline our plan to study organic monolayer/layered inorganic semiconductor hybrid systems to explore and exploit the effects of (patterned) monolayer adsorption on the unique electronic properties these layered semiconductors.

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Poster A6

SIMULATIONS OF THE ANGLE-RESOLVED PHOTOEMISSION FOR BENZENE ON Pd(110)

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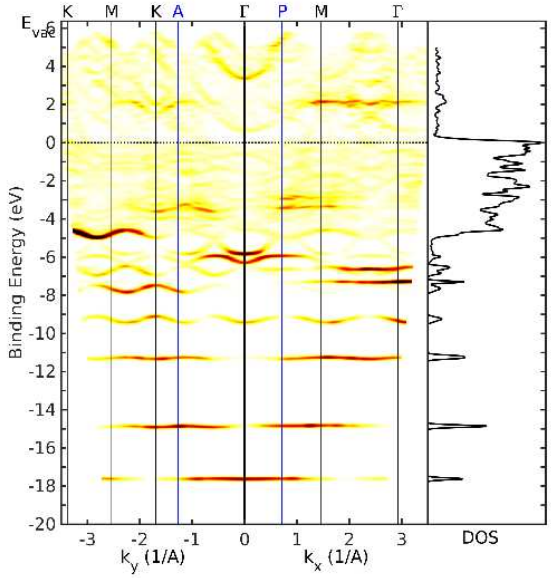
Angle-resolved photoemission spectroscopy (ARPES) is a powerful technique to investigate the electronic structure of organic films at the interface to metallic surfaces. However, the experimental data is sometimes difficult to interpret owing to photoemission selection rules which depend on the chosen experimental geometry such polarization vector, angle of incidence and photon energy of the incoming light. Therefore, ARPES simulations based on ab-initio calculations within the framework of density functional theory (DFT) are of great interest. A particularly simple and at the same time powerful approach is to approximate the final state by a plane wave. This renders the ARPES data to be proportional to the Fourier transform of the initial state leading to a technique sometimes termed orbital tomography [1]. Thereby, detailed information on the spatial distribution of the initial state orbital can be obtained. However, the validity of the plane wave approximation has been questioned, in particular, in the limit of small molecules [2].
Therefore in this contribution, I investigate the electronic structure of a benzene ring adsorbed on a Pd(110) surface. After exploring the energetically most favorable adsorption sites by making use of state-of-the-art van-der-Waals corrected DFT calculations, I perform ARPES simulations for several substrate-adsorbate-geometries. When compared to experimental data, the adsorption-site sensitivity which is found in theoretical results allows us to draw conclusions on the optimum adsorption site and orientation of benzene on Pd(110). We discuss the applicability of the plane wave approximation for the final state for such rather small molecules and present an approach which allows us to go beyond the plane wave approximation.



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Poster A7

ADSORPTION OF ORGANIC MOLECULES ON GRAPHENE

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Graphene is a two dimensional allotrope of carbon with a honeycomb lattice structure and several unique electronic and optical properties. Our study deals with understanding the interaction of organic adsorbates on graphene namely Pyridine, (C_5H_5N) and 4, 4'-bipyridine, $(C_5H_5N)_2$. The stable adsorption configurations of these molecules are determined by density functional theory considering van der Waals correction, taking into account the translational as well as rotational degrees of freedom. Pyridine placed parallel to the graphene sheet, with its nitrogen atom at the center of the graphene ring is found to be the most stable configuration, with an adsorption energy of -0.60 eV in agreement with results in the literature [1]. In gas phase, 4,4'-bipyridine has a torsional angle of 33° which reduces significantly (to about 19°) when placed on graphene. The stable configuration is when the pyridyl rings of the molecule follow a similar stacking as found in graphite.
The electronic band structure and the density of states of pyridine adsorbed on graphene reveals little interaction of the molecule with the substrate. The spatial overlap of the molecular orbitals with the substrate bands induces an energy broadening of their features in the density of states as seen in Figure 1. Such width can be related to the electron transfer times at the molecule/graphene interface which is in the order of few femtoseconds to a few hundred femtoseconds for different orbitals. Core level spectroscopies are addressed by examining the near-edge X-ray absorption fine structure (NEXAFS) spectrum of the system using the transition-potential approach [2, 3]. The effect of a metal substrate supporting graphene is eventually studied by considering these organic molecules adsorbed on graphene placed on nickel (111).

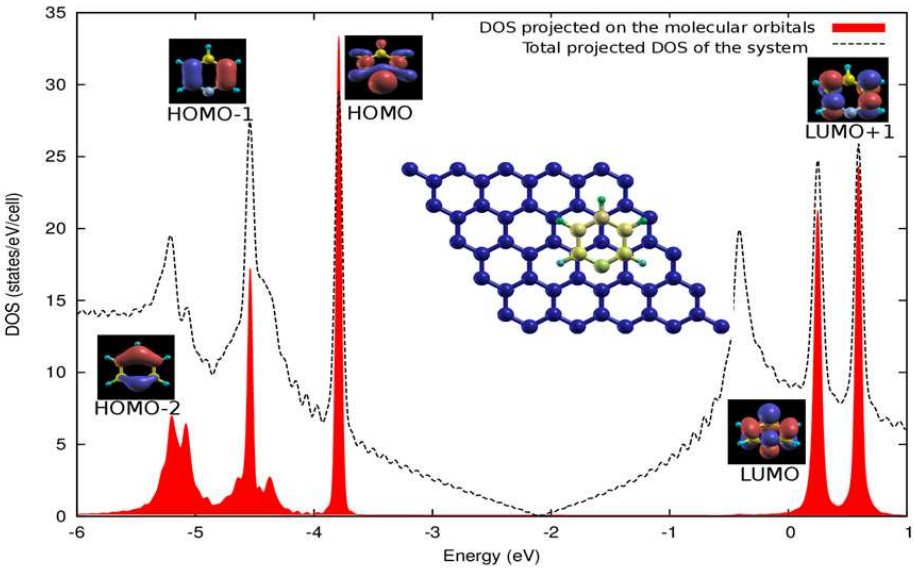

Figure 1: The density of states of pyridine adsorbed graphene and the density of states projected on the molecular orbitals (red), arranged from HOMO-2 to LUMO+1. Inset shows the molecular orbitals of pyridine in gas phase.

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Poster A8

RELIABLE ENERGY LEVEL ALIGNMENT AT PHYSISORBED MOLECULE-METAL INTERFACES FROM DENSITY FUNCTIONAL THEORY

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A key physical quantity for nanostructured molecule-metal junctions is the energy level alignment of molecular electronic states with the Fermi level of the metal. Here, we develop and apply an efficient theoretical method, based on density functional theory (DFT), which can yield quantitatively accurate energy level alignment for physisorbed metal-molecule interfaces.[1] It builds on the "DFT+Σ" approach, grounded in many-body perturbation theory, which introduces an approximate electron self-energy for correcting the level alignment obtained from conventional DFT for missing exchange and correlation effects associated with the gas-phase molecule and substrate polarization. We extend the "DFT+Σ" approach in two important aspects: first, we employ optimally-tuned range-separated hybrid functionals to compute the gas-phase term, rather than rely on GW or total energy differences as in prior work; second, we use a non-classical DFT-determined image-charge plane of the metallic surface to compute the substrate polarization term, rather than the classical DFT-derived image plane used previously. The approach is validated by a detailed comparison with experimental and theoretical reference data for several prototypical molecule-metal interfaces. We show that our method allows for obtaining quantitatively accurate energy level alignment information from DFT. In particular, it correctly captures level alignment trends across chemical systems and retains its accuracy even for molecules for which conventional DFT suffers from severe self-interaction errors.

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Poster A9

EFFECT OF DEPOLARIZATION IN THE PACKING OF SELF-ASSEMBLED MONOLAYERS

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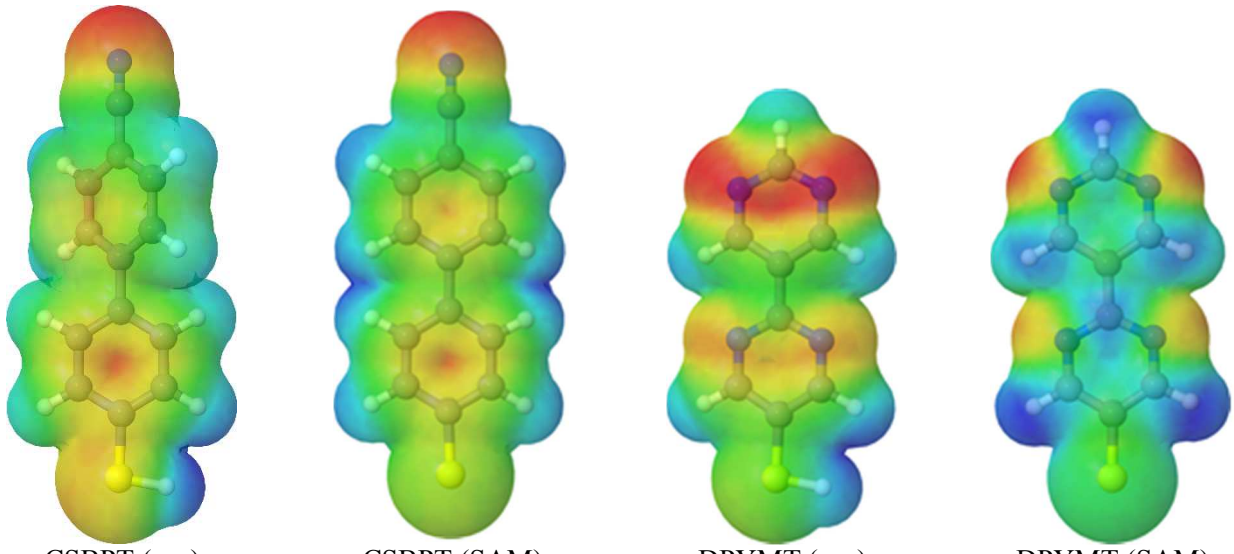
In this study we present an algorithm for the calculation of atomic charges to be used in atomistic force fields. This method is specifically tailored to take into account the effect of the molecular depolarization, which takes place when an ordered arrangement of tightly packed molecules is brought together, as in case of self-assembled monolayers (SAM) on gold surfaces. We employed atomistic molecular dynamics (MD) simulations to study the packing geometry of four SAM-yielding molecules. The resulting geometry was used to compute atomic charges at the DFT level of theory by including explicitly a background charge distribution mimicking the interactions with neighboring molecules. We found a reduction of the molecular dipole of about a factor 2 compared to the same molecule in gas phase. This procedure is iterated until self-consistency is achieved between ab-initio atomic charges and the resulting MD packing geometry.



CSBPT (gas) CSBPT (SAM) DPYMT (gas) DPYMT (SAM)

Figure 1. Molecular electrostatic potential of two SAM-yielding molecules in gas and condensed (SAM) phase, computed at the DFT level of theory.

Poster A10

THYMINE ADSORBED ON THE SILICON(001) SURFACE: ATOMIC AND ELECTRONIC PROPERTIES

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The study of electronic and optical properties of organic – and in particular prebiotic – molecules adsorbed on surfaces is relevant both for solid state physics and for astrochemistry and astrobiology. Adsorption of organic polyfunctional molecules on semiconductor surfaces allows to tune the surface electronic properties according to the character of the interface chemical bonding [e.g. 1,2]. In particular, the interaction of organic molecules with silicon surfaces is of interest because of the potential applications in molecular electronics and biosensors [e.g. 3,4]. On the other hand, the knowledge of how the electronic and optical properties of prebiotic molecules change when they are adsorbed on solid surfaces, with respect to the gas phase, may be relevant for theories on the origin of life.

In this work, atomic and electronic properties of thymine (a pyrimidinic nucleobase) adsorbed on the silicon(001) surface were investigated within a plane-wave (PW) density functional theory (DFT) approach (using the Abinit code [5]), and compared with those of other similar adsorbate systems, such as tert-butanol [6] or uracil [2,7] on the same substrate.

Moreover, we calculated the electronic and optical properties of the isolated molecule using an all-electron Gaussian-based code (NWChem [8]). Using DFT and time-dependent DFT we computed electron affinities and first ionization energies, quasiparticle correction to the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap, electronic absorption spectra and excitonic effects [9]. These results allowed us to compare the isolated molecule electronic properties with those for thymine adsorbed on the Si(001) surface.

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Poster A11

GROWTH AND DOPING OF ULTRATHIN LAYERS OF TETRAPHENYLDIBEZNOPERIFLANTHENE (DBP)

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The dye molecule tetraphenyldibenzoperiflanthene (DBP) is a promising candidate for usage in OPVCs and OLEDs. Its aromatic backbone is formed by the DIP molecule with two additional benzene rings and four phenyl substituents. In order to investigate growth and doping processes as well as the optical properties of DBP thin films (sub-monolayers to ~10 monolayers) on various substrates, *in situ* differential reflectance spectroscopy (DRS) [1,2] measurements were performed. A strong interaction between molecules and single crystalline metal surfaces was found, where structural characterization by low energy electron diffraction (LEED) and low temperature scanning tunneling microscopy (LT-STM) at 1 K revealed a well ordered flat lying thin film growth in a herringbone arrangement within the first monolayer (see Fig. 1). Depending on the coverage two distinct spectral fingerprints of DBP molecules arise indicating a transition from DBP monomers to aggregates. Additionally DBP films on mica and Ag(111) were doped by potassium deposition, where a formation of anions and dianions was identified by its strong impact on the optical properties.

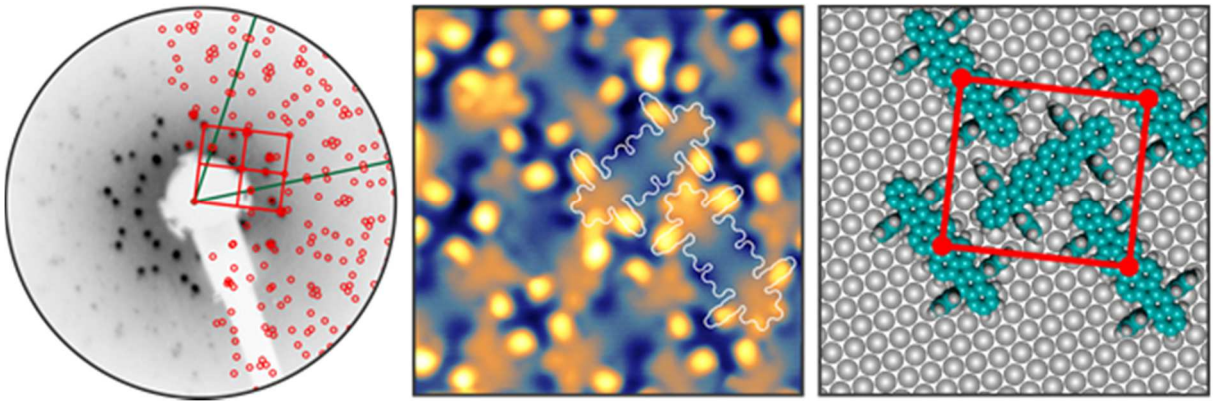

Figure 1. Structure of 0.7 MLE DBP on Ag(111). a) LEED measurement at an electron energy of 21.5 eV. The primitive reciprocal substrate directions (green) as well as simulated LEED spots for the adorbate lattice with the corresponding reciprocal unit cell (red) are shown. b) LT-STM image (5 × 5 nm2, UB = -1.5 V, IT = 5 pA) of DBP molecules in the first ML showing a herringbone arrangement. c) Structure model for adsorption of DBP on Ag(111) with Ag(111) lattice points and the adsorbate unit cell (red).

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Poster A12

STOICHIOMETRY-DEPENDENT STRUCTURAL REORDERING PROCESSES OF PTCDA MONOLAYER DOMAINS ON Ag(111) UPON K INTERCALATION

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Alkali metals are frequently used for simple yet efficient n-type doping of organic semiconductors. However, the incorporation of dopants from the gas phase into molecular crystal structures needs to be controlled and well understood in order to optimize the electronic properties (charge carrier density *and* mobility) of the target material. Here, we report that potassium intercalation into pristine 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) monolayer domains on a Ag(111) substrate induces distinct stoichiometry-dependent structural reordering processes, resulting in highly ordered and large K_xPTCDA domains. The emerging structures are analyzed by low temperature scanning tunneling microscopy (STM), scanning tunneling hydrogen microscopy (STHM) [1], and low energy electron diffraction (LEED) as a function of the stoichiometry x = K : PTCDA. STM simulations based on density functional theory (DFT) combined with the Tersoff-Hamann approach are performed on slabs with varying adsorbate structures. They turn out to be essential for a correct interpretation of the experimental ST[H]M data. The epitaxy types for all doped stages are determined as point-on-line; and K adsorbs in the vicinity of the carboxylic and anhydride oxygen atoms of the PTCDA molecules for both K_2PTCDA and K_4PTCDA (Fig. 1). The observed intercalation-induced reordering indicates an altering of the bonding mechanisms of the pristine PTCDA film initially strongly hybridized with the Ag(111) substrate.

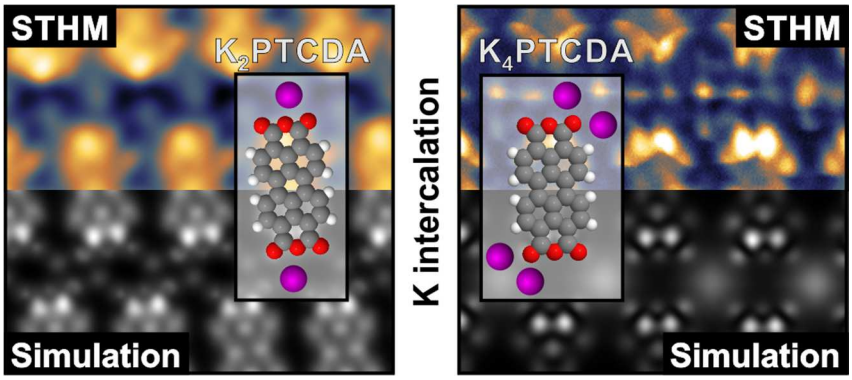

Figure 1. Measured STHM and simulated STM images of K intercalated PTCDA on Ag(111) for the stoichiometries K_2PTCDA (left) and K_4PTCDA (right). The corresponding structure models are superimposed.

[1] R. Temirov, S. Soubatch, O. Neucheva, A. C. Lassise, and F. S. Tautz. *New J. Phys.* **10** 053012 (2008).

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Poster A13

LEEM INVESTIGATION OF STRUCTURE AND GROWTH OF HETEROMOLECULAR LAYERS ON NOBLE METAL SURFACES

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The first organic layer grown on a metal substrate is crucial for the performance of organic electronic devices since it determines the growth and structure of the subsequent film and influences the charge transport between the electrode and the active organic layer. We investigated such systems by depositing the molecules copper-II-phthalocyanine (CuPc) and 3,4,9,10-perylen-tetracarboxylic-acid dianhydride (PTCDA) on Ag(111) and Cu(001) in heteromolecular layers. These two molecules were chosen since they represent a typical donor-acceptor model system for organic electronics.
Different heteromolecular structures were identified on both surfaces and LEED was applied to determine their geometric structure. The growth of the heteromolecular layers was studied intensively with the LEEM instrument [1,2]. The experiments showed that the deposition order of the molecules does not influence the final structure on Ag(111) [1], while it determines the structure formed on Cu(001). The reason for this is that the stronger interaction of the molecules with copper compared to silver leads to a lower mobility and, thus, the formation of heteromolecular layers is hindered on Cu(001) in certain cases. Nonetheless, heteromolecular structures could be produced by the right deposition order and substrate temperature during the deposition.

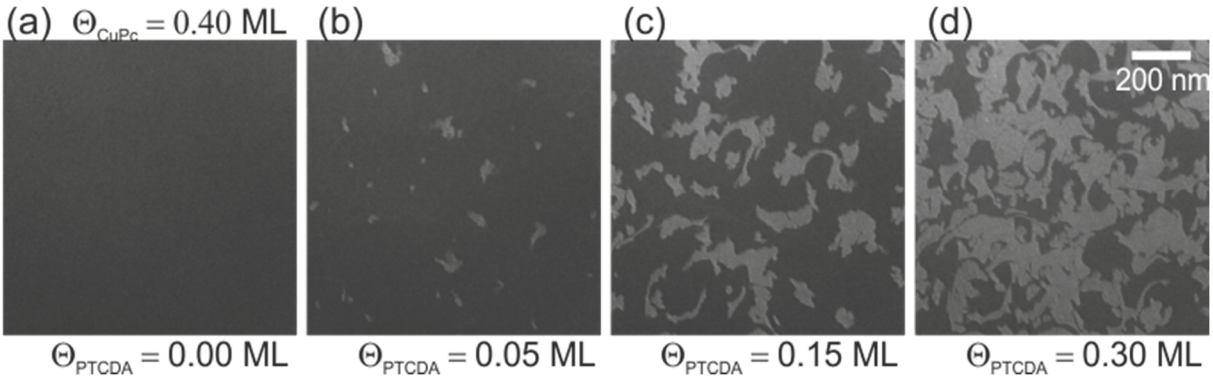

Figure 1. LEEM images taken during the deposition of PTCDA on a submonolayer film of CuPc on Ag(111). (a) The homomolecular CuPc film forms a disordered dilute phase on the surface leading to a homogeneous contrast. (b) Heteromolecular islands (bright contrast) start to grow shortly after the deposition of PTCDA has been started. (c) The islands continue to grow until the deposition of PTCDA is stopped (d).

[1] B. Stadtmüller, C. Henneke, S. Soubatch, F. S. Tautz, C. Kumpf, *New J. Phys.* **17** 023046 (2015).
[2] T. Duden, A. Thust, C. Kumpf, F.S. Tautz, *Microsc. Microanal*. **20** 968-973 (2014)

Poster A14

INFLUENCE OF THE CENTRAL METAL ATOM ON PHTHALOCYANINE-BASED HETEROMOLECULAR MONOLAYERS: COMPARISON OF CuPC+PTCDA AND SnPC+PTCDA ON THE SILVER (111) SURFACE

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Understanding the interface between organic semiconductors and metal contacts is of vital importance to the field of organic electronics. For example, it can affect the carrier injection and extraction barriers as well as the growth behavior of the active layer. For this reason, much research has been done on the properties of so-called monolayers, single-molecule thick layers of prototype organic semiconductors such as aromatic anhydrides[1] and phthalocyanines[2], many of which display complex behavior on weakly interacting metal surfaces, such as those of silver, gold and copper.
Thus far, most research has been focused on monolayers consisting of only one type of molecule. However, since in many devices the active layer consists of a blend of multiple molecules, additional research is needed to understand the interplay between these molecules. Recently it has been shown that in monolayers consisting of two organic molecules, the electronic properties of these molecules, as well as their interaction with the surface can differ significantly from those in the monomolecular phases[3].
Phthalocyanines form a very interesting class of components for these mixed monolayers since their interaction with the substrate, as well as their electronic properties can be tailored by exchanging the central metal atom. This process does not significantly affect the lateral interaction between these phthalocyanines and other molecules in the monolayer, thereby allowing the isolation of the influence of the metal-molecule interactions from the molecule-molecule interactions.
We present a comparison between two phtalocyanine-containing mixed monolayers on the silver (111) surface, consisting of either tin phthalocyanine (SnPc) or copper phtalocyanine (CuPc) mixed with mixed with the aromatic anhydride PTCDA. The SnPc+PTCDA system displays a variety of ordered phases very similar to those found in the CuPC+PTCDA system but there are subtle differences due to a stronger interaction between SnPc and the underlying metal surface. In one phase of both systems, the so-called mixed brick wall phases (MBW), the molecules order in exactly the same way relatively to each other and this is therefore an ideal model system to study the influence of the central metal atom of the phthalocyanine on the PTCDA molecules. Through a variety of measurements on this phase it is shown that, although exchanging the central metal ion does not change the lateral ordering, the vertical adsorption geometry of the PTCDA molecule is strongly affected by the exchange.

[1] Martin Willenbockel et al. *Physical Chemistry Chemical Physics* **17** (2014)
[2] Benjamin Stadtmüller et al. *Physical Review B* **83** (2011)
[3] Benjamin Stadtmüller et al. *Nature Communications* **5** (2014)

Poster A15

MEASURING THE EFFICIENCY OF PLASMON EXCITATION BY TUNNELLING CURRENTS

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The fact that light is emitted when a current is injected through a tunnel junction was first found in the 70's by Lambert and McCarthy [1], and is currently exploited to analyze the light arising from the local junctions created between the tip and the sample in Scanning Tunneling Microscopes (Scanning Tunneling Luminescence, STL) [2]. It was long understood that the origin of the light is the radiative decay of Localized Surface Plamon Resonances (LSPRs) which are excited by electrons tunneling inelastically between the electrodes. However, the relatively large energies of LSPR modes hindered any experiment aimed at measuring the inelastic signal in I(V) curves recorded while tunneling (Scanning Tunneling Spectroscopy, STS). In this contribution we show STS measurements displaying a clear inelastic signal in the same energy range as the light recorded in STL experiments with the same tip. Our experiments allow for a quantification of the plasmon excitation efficiency by tunneling electrons which might become essential to extract information from STL spectra.

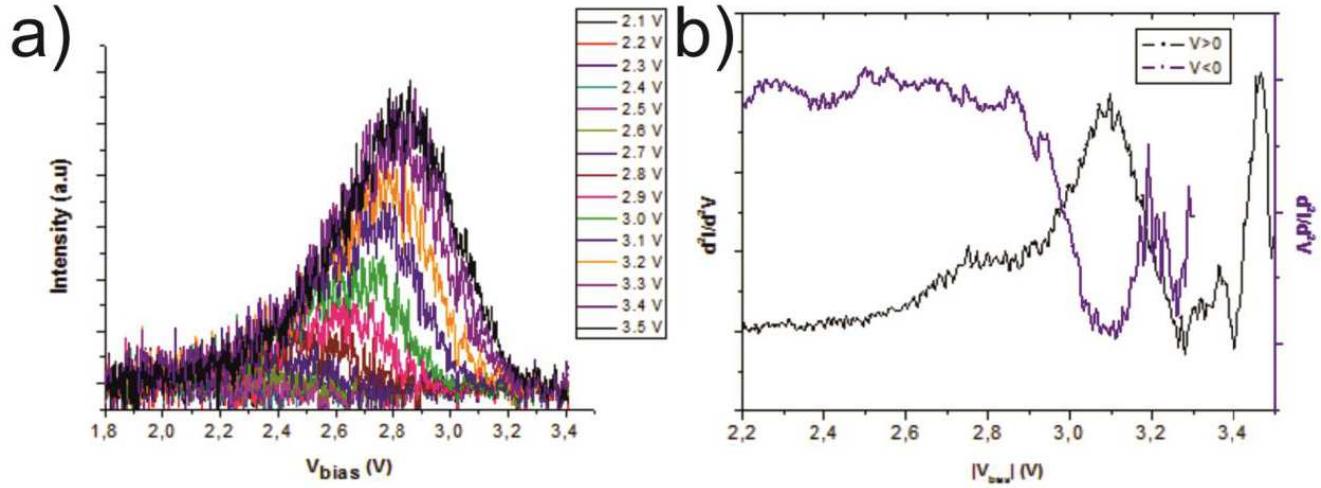

Figure 1. a) STL spectra recorded at different bias voltages. b) STS spectra revealing an inelastic excitation at around 3 eV

[1] J. Lambert, S. L. McCarthy, *Phys. Rev. Lett.* **57** 923 (1976).
[2] F. Rossel, M. Pivetta, W.-D. Schneider, *Surf. Sci. Rep.* **65** 129 (2010)

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Poster A16

ORBITAL TOMOGRAPHY OF HYBRIDIZED AND DISPERSING MOLECULAR OVERLAYERS

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With angle-resolved photoemission experiments and ab initio electronic structure calculations, the pentacene monolayers on Ag(110) and Cu(110) are compared and contrasted, allowing the molecular orientation to be determined and an unambiguous assignment of emissions to specific orbitals to be made. On Ag(110), the orbitals remain essentially isolated-molecule-like, while strong substrate-enhanced dispersion and orbital modification are observed upon adsorption on Cu(110). We show how the photoemission intensity of extended systems can be simulated and that it behaves essentially like that of the isolated molecule modulated by the band dispersion due to intermolecular interactions.

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Poster A17

PARA-HEXAPHENYL AS A MOLECULAR SENSOR OF SURFACE QUALITY: INFLUENCE OF ION BEAM IRRADIATION AND AIR PASSIVATION OF TiO_2(110)

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We report on molecular ultrathin films growth on titanium dioxide single crystal surfaces, either atomically flat or ion beam modified. We use the *para*-hexaphenyl (6P) molecule as a molecular sensor of surface quality. Flat-lying, parallel to the substrate orientation of molecules indicates a flat, stoichiometric surface whereas upright-standing behavior correlates with surface disturbance.
The surface morphology of the developed structures was extensively studied: *in situ* by means of non-contact AFM and *ex situ* by tapping-mode AFM and SEM.
The surface structure of titanium dioxide has been investigated for a long time and is relatively well known [1]. Oxygen rows forming a (1x1) reconstruction make it a perfect anisotropic template for molecular growth. The chain-like, anisotropic structure of *para*-hexaphenyl molecules induces different optoelectronic properties for various herringbone structure crystallite orientations [2].
The atomically flat TiO_2(110)(1x1) surfaces were prepared in UHV by cycles of Ar+ sputtering and subsequent annealing. Some of samples underwent eventually cycles of additional ion beam bombardment which resulted in certain surface roughness, either isotropic or anisotropic (*ripples*).
For atomically flat substrate the formation of tens of micrometers long 6P nanoneedles composed of lying molecules is observed. Subsequent air exposure initiates a dewetting process resulting in the formation of the small features between the nanoneedles – crystallites. When the procedure is reversed – exposure precedes the deposition, it results in the formation of dendritic islands, composed of upright standing molecules. (The existence of a 6P wetting layer was observed previously on mica(001) [3] and Cu(110) (2x1)-O [4]. The presented research involving *ex situ* and *in situ* measurements provides direct proof that a similar concept holds for titanium dioxide.)
Ion beam irradiation of titanium dioxide surface disturbs molecule-substrate interaction causes para-hexaphenyl molecules to form upright-standing islands. Tailoring the surface properties: anisotropy, height and lateral size of surface structures, we change the molecular islands size, shoreline and degree of attachment.

[1] U. Diebold, *Surface Science Reports* **48**(5-8) 53–229 (2003)
[2] G. Hlawacek et al, *J. Phys.: Condens. Matter* **25**(14) 143202 (2013)
[3] L. Tumbek et al, *Phys Rev B* **86** 085402 (2012)
[4] J. Fleming et al, *J. Phys.: Condens. Matter* **21**(44) 445003 (2009)

Poster A18

$LuPC_2$ ON Au(111) EXPOSED TO GASES

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Rare-earth Phtalocyanines are very promising molecules due to their interesting electronic properties which make them ideal candidates for many different applications: from gas sensing to organic devices. However little is still known about their structure when deposited as thin films and their reactivity toward atmospheric gases.
We have deposited Lutetium bis-Phtalocyanine ($LuPc_2$) thin films on Au(111) in Ultra High Vacuum (UHV). We then characterized the interaction between the surface and the substrate by means of X-ray Photoelectron Spectroscopy (XPS) and Near-Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy, and the structure by Scanning Electron Microscopy (STM) and Grazing-Incidence X-ray Diffraction (GIXRD). With GIXRD, we are able to show that molecules self-organize in a perfectly 2D square structure and we can determine the respective orientation of the supramolecular film with respect to Au(111) crystallographic directions. By XPS and NEXAFS, we report a limited interaction between the substrate and the overlayer and evidence an in-plane orientation of the molecules. Moreover, reactivity of the film to atmospheric gases (mainly O_2) has shown that O_2 molecules physisorb on the molecular film at liquid nitrogen temperatures and desorb around 100 Kelvins. It appears that the physisorption is associated to a charge transfer between the phtalocyanine and the oxygen that only affects the ligand.

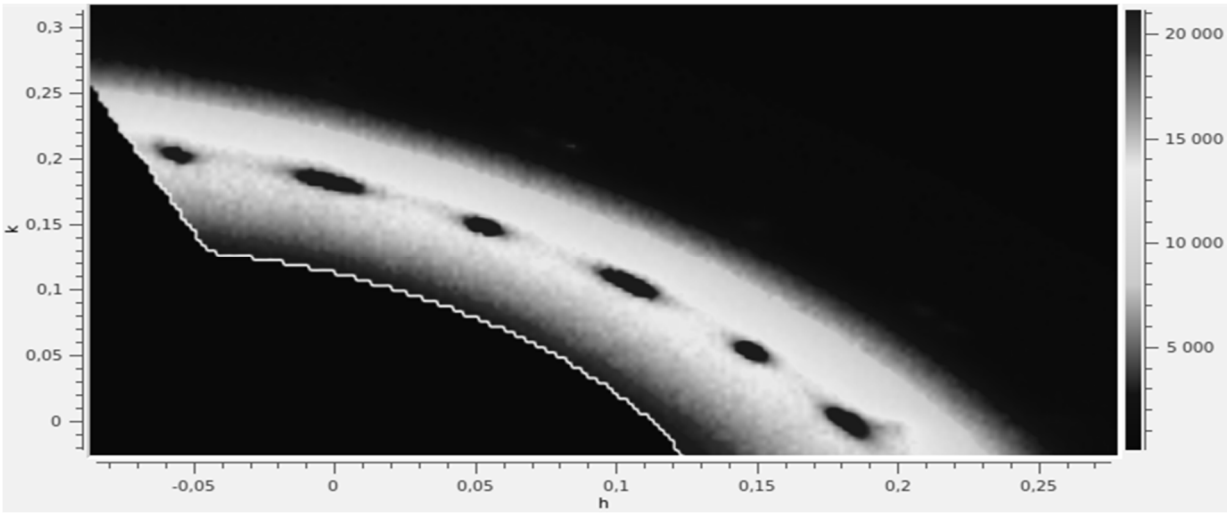

Figure 1. GIXRD image of $LuPc_2$ grown on an Au(111) surface

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Poster A19

ANTIMICROBIAL ACTIVITY OF QUATERNARY AMMONIOUM-GRAFTED MCM-48 AND LOADED WITH BIOCIDE

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In the present work, surface modified mesoporous silica nanoparticles (MSNs) with quaternary ammonium salts (QAS) and loaded with the biocide Parmetol S15 were synthesised as functional fillers for antifouling coatings for marine applications. From the family of the M41S, MCM-48 was selected as carrier due to its cubic structure and its interesting physical properties such as high surface area and specific pore volume[1]. Several studies have concluded that QAS can be considered excellent candidates for antimicrobial agents because of their environmentally friendly performance, effective biocidal activity and long term durability[2]. The QAS used for the surface modification of the MCM-48 was the 3-(trimethoxysilyl)-propyldimethyloctadecylammonium chloride.
The MCM-48 were synthesised in room temperature conditions according to the method of Schumacher et al[3]. The SEM images have shown that spherical nanoparticles with variation of size between 200 and 500 nm were obtained (Figure 1a). The specific surface area, the average pore diameter and the specific pore volume were calculated to be 924 m^2/g, 3.1 nm and 0.69 cm^3/g respectively. FTIR, TGA (Figure 1b) and Z-potential measurements have shown that the attachment of the QAS at the surface of the MCM-48 was successful. The Z-potential measured at pH 7.8 for the modified NPs shifted to 61.2 mV due to the positively charged quaternary ammonium groups, whereas that of pristine silica was -34.2 mV due to the negatively charged hydroxyl groups at the silica surface. In the following period, experiments will be run to study the encapsulation of the biocide inside the MCM-48 and the biocidal activity of the modified NPs.

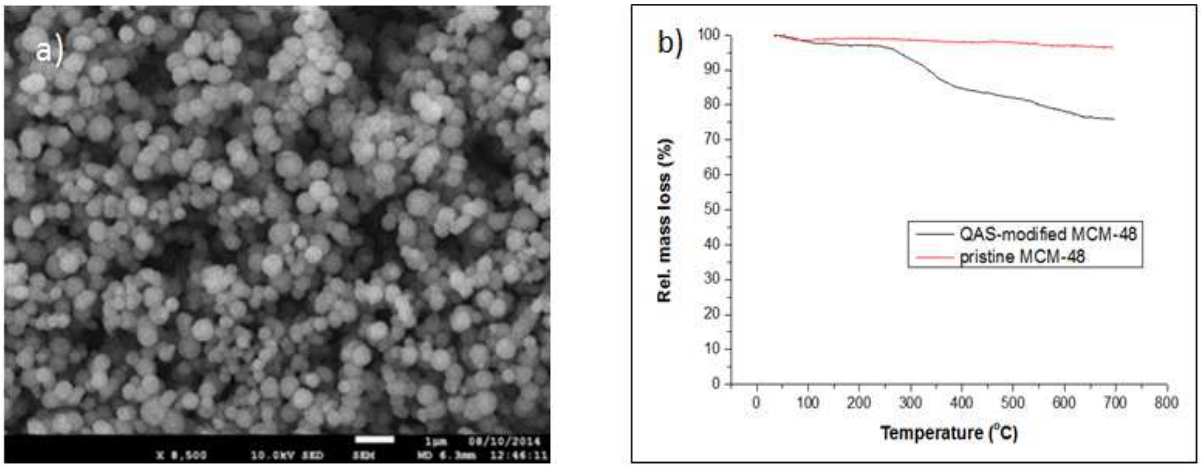

Figure 1. a) SEM image of pristine MCM-48, b) TGA curves of pristine and QAS-modified MCM-48.

[1] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature* **359** 710 (1992).
[2] J. Song, H. Kong, and J. Jang, *Colloids Surfaces B Biointerfaces* **82** 651 (2011).
[3] K. Schumacher, M. Grün, and K. Unger, *Microporous Mesoporous Mater.* **27** 201 (1999).

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Poster A20

A MODEL OF CHITOSAN-MODIFIED CALCIUM-PHOSPHATE NANOPARTICLES AS AN ORAL DRUG DELIVERY SYSTEM

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Calcium-phosphate nanoparticles are investigated as a model to cross Caco-2 cell monolayers at physiologic pH, testing also the effect of diethylene triamine pentaacetic acid-chitosan (DTPA-Chitosan) on their permeability.
This kind of particles has peculiar properties, such as organic solvent free synthesis, high biocompatibility and biodegradability and the release of the cargo molecule at low pH (<5), typical of endosomal or tumoral environment [1]. For these promising characteristics, they are exploited mainly in transfection, gene delivery and gene silencing with DNA, si-RNA or mi-RNA delivery [2].
An innovative modification of this nanocarrier with DTPA-Chitosan is tested to improve the nanoparticle absorption through the intestinal epithelium to investigate their application for oral delivery.
Calcium phosphate nanoparticles (10%v/v) encapsulating fluorescein isothiocyanate–dextran are synthesized and then stabilized by sodium citrate (100mM) to 70-100nm. DTPA-Chitosan (0.05% w/v) and citrate (100mM) are formulated with the calcium-phosphate nanoparticles. Caco-2 cell monolayers are used as model to test the permeability of calcium-phosphate nanoparticles in different formulations and their passage is quantified by fluorescence intensity.
The nanoparticles are able to cross the Caco-2 monolayer and the absorption enhancing effect of DTPA-Chitosan is significant: the cumulative percentage transport of DTPA-Chitosan (0.05% w/v) treated calcium phosphate nanoparticles (3.7%) has 2.5-fold increase compare to non-treated formulation (1.3%). The reduction (58±5%) in transepithelial electrical resistance indicates that DTPA-Chitosan facilitates the transport of calcium phosphate nanoparticles by opening tight junctions between Caco-2 cells; this mechanism of action is a well-known property of chitosan whereby it is an absorption enhancer.
In conclusion calcium phosphate nanoparticles represent a versatile and encouraging drug delivery system; in particular, this study highlights their capability to cross the intestinal epithelium further enhanced by DTPA-Chitosan, supporting the promising ability of this system as an oral absorption vehicle.

[1] V. Sokolova, O. Rotan, J. Klesing, P. Nalbant, J. Buer, T. Knuschke, A. M. Westendorf, M. Epple *J Nanopart Res* **14** 910 (2012)
[2] Hou S, Ma H, Ji Y, Hou W, Jia N. A. *ACS Appl. Mater. Interfaces* **5**(3):1131-1136 (2013)

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Poster A21

COMPLEX BEHAVIOUR OF CAFFEINE CRYSTALLITES ON SOLID SURFACES

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Defined fabrication of organic thin films by physical vapor deposition (PVD) are highly desired in applications allowing adjustments of polymorphic and morphological properties. Most PVD studies on organic films focus on conjugated molecules, as these promise a direct application in electronics. However, for other molecules, especially drug molecules, such studies are rare. Anyway, drug molecules are very interesting as they feature asymmetric chemical structures with somehow ambipolar character. This ensures aqueous solubility and penetration abilities to the living cell. Furthermore, such molecules might allow fundamental information of heterogeneous crystal growth to be obtained.

Within this work, the growth of a prototype asymmetric, disk-like molecule (caffeine) on silica, muscovite mica and NaCl surfaces is studied. Microscopy reveals, independent of the substrate, the presence of needle-like crystallites after the PVD process in a Hot-Wall-Epitaxy setup (HWE). X-ray diffraction reveals, that for all samples a unique polymorph, β-form, is present with caffeine arranging in an edge-on conformation. Depending on the surface, the azimuthal arrangement, however, is different. A random distribution is present on silica, while mica as well as NaCl induce defined azimuthal needle directions during growth (see Figure 1). This agrees with their different surface properties, i.e. isotropic properties are present on silica while the others have regular surfaces. Thus the caffeine needles (or molecules) adapt arrangements on account of the specific surface properties which is further concluded from X-ray diffraction pole figure measurements.

Defined variation of the HWE process parameters and the surfaces reveal that the quality of needle alignment is strongly affected by the surface indicating a route for high quality heterogonous crystallisation. Comparison of previous studies,[1] on solution cast caffeine show that the needle quality is higher for the HWE process. Solution casting also allows for azimuthal alignment but due to different environmental conditions, needles align along different directions compared to the HWE processed needles.

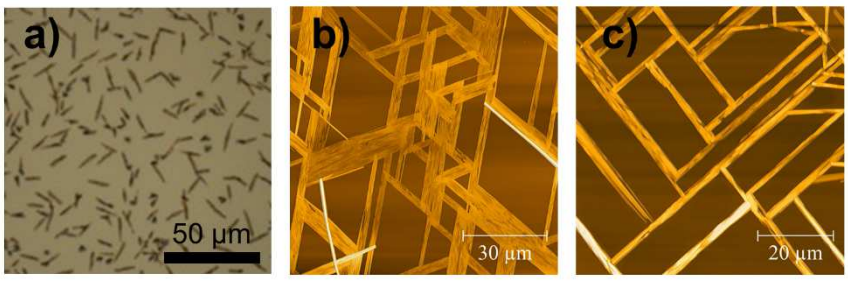

Figure 1. a) Optical micrograph showing azimuthally randomly distributed caffeine needles on silica and atomic force microscopy height images of bi-axially aligned needles on muscovite mica (b) and NaCl (c).

[1] Werzer, O. et al. *Cryst. Growth Des.* **13** 1322–1328 (2013).

Poster A22

PROTEIN-ASSISTED ONE POT SYNTHESIS AND BIOFUNCTIONALIZATION OF GOLD NANOPARTICLES FOR SELECTIVE TARGETING OF CANCER CELLS

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An innovative one-step synthesis and biofunctionalization of gold nanoparticles (AuNPs) with a non-immunogenic engineered B domain variant of protein A (spaBC3) as biotemplate capable of interacting with gold surface and participating in site-specific conjugation of antibodies was developed [1]. The synthesis conditions were compatible with protein requirements allowing the preservation of the protein structure in a wide pH range. The dimension and morphology of nanoconjugates were tuned varying the Au/spaBC3 and Au/BH_4^- molar ratios giving the nanoparticles with SPR band in a 514-520 nm range. The optimal conditions (spaBC3/$AuCl_4^-$ ratio of $2.5 \cdot 10^{-4}$:1) resulted in spherical AuNPs of 6.2 ± 1.2 nm with an average of 2-4 molecules attached to the nanoparticle surface. The residual surface of Au-spaBC3 nanoconjugates was covered by PEG-SH molecules to protect them from nonspecific adsorption and to increase their stability, even in 6 M NaCl solution. To assess the extent of preserved bioactivity of the bound spaBC3, we used trastuzumab (TZ), a humanized monoclonal antibody possessing a high affinity toward HER2-positive breast cancer cells. Moreover, it was found that Au-spaBC3 specifically recognized TZ. Targeting efficiency of Au-TZ toward HER2 was studied using MCF7 (HER2+) and MDA (HER2–) cells both by flow cytometry and confocal microscopy. Flow cytometry revealed a good labeling efficiency of Au-TZ toward HER2+ cells. Confocal microscopy showed the absence of any fluorescence signal of MDA cells incubated for up to 1 h, while Au-TZ were observed inside the MCF7 cells indicating the completion of their penetration, while free TZ was still mostly localized on the outer membrane, suggesting a marked increase in cell entrance assisted by nanoparticles.

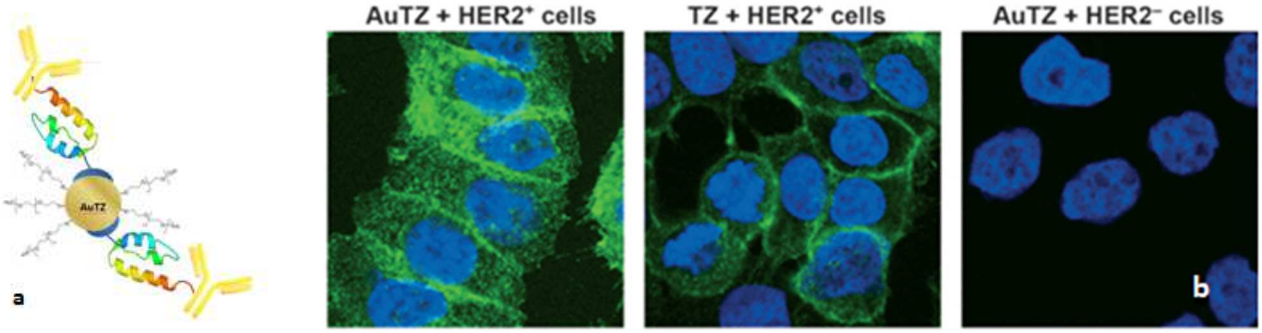

Figure 1. (a) Model of gold nanoconjugates functionalized with the protein spaBC3 and the mAb Trastuzumab (AuTZs) for selectively targeting of HER2 receptors overexpress in MCF7 cancer cells. (b) Confocal images of MCF7 (HER2+) after 1 h of incubation with AuTZs, TZ incubated with MCF7 as CTRL+, AuTZs incubated with MDA (HER2–) as CTRL–. (TZ in green and nuclei in blue).

[1] Miriam Colombo, Serena Mazzucchelli, Veronica Collico, Svetlana Avvakumova, Laura Pandolfi, Fabio Corsi, Francesca Porta, and Davide Prosperi, *Angewandte Chemie* **51**(37) 9272–9275 (2012).

Poster A23

BIOCOMPATIBLE NANOVECTORS FROM SELF-ASSEMBLED AMPHIPHILIC BLOCK COPOLYMERS FOR BRAIN MEDICINE APPLICATIONS

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Among various body diseases, disorders of the central nervous system (CNS) remain troublesome to treat. One of the major difficulties encountered in delivering drugs to the brain is the fact that the potential agent must be able to cross the blood-brain barrier (BBB), a very specialized system of endothelial cells that separates the blood from the brain cells, protecting the CNS from potential hazardous substances present in circulation. Unfortunately, it also prevents the penetration of nearly 100% of therapeutic agents [1]. A promising strategy to successfully enhance the CNS penetration of therapeutics is based on nanovectors, drug-carrying nanoparticles that can be properly functionalized on their surface to interact with the BBB cells at the molecular level and to enhance the barrier crossing by exploiting the existing physiological mechanisms of transport.

In this study, we present the preparation and functionalization of polymeric nanoparticles for drug incorporation and transport across the BBB. Amphiphilic block copolymers are known for their ability to spontaneously organize in a variety of diverse morphologies, ranging from micelles to vesicles and other structures of higher complexity, when in contact with a selective solvent for one of the blocks [2]. The block copolymer of choice for the present investigation is poly(N,N'-dimethylacrylamide)-block-polystyrene (PDMA-*b*-PS), a suitable system for the formation of drug delivering NP: depending on the overall chain length and on the hydrophilic fraction, they can organize in highly monodisperse core-corona micelles [3].

Thus, six different PDMA-*b*-PS NPs were synthesized by RAFT with a variety of total molecular weight and ratios of the two blocks, and assembled with an optimized method involving gradual variation of the solution environment and dialysis. $PDMA_{86}$-*b*-PS_{241}, the most suitable copolymer for bio applications in terms of NP size and cytotoxicity, was selected for functionalization with mApoE peptide (Fig. 1), which enhanced its permeability through the BBB.

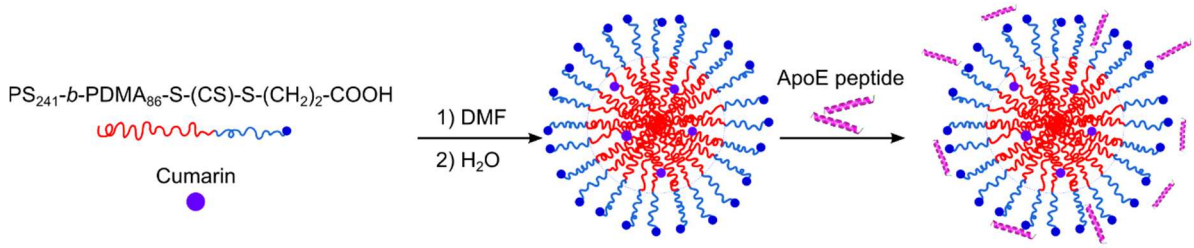

Figure 1. Self-assembly and functionalization of $PDMA_{86}$-*b*-PS_{241} NPs for drug delivery across the BBB.

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Poster A24

PROTEIN STRUCTURAL CHANGES INDUCED BY INTERACTIONS WITH THE SURFACE OF COLLOIDAL NANOPARTICLES

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Current progress in nanotechnologies have led to an extensive use of nanoparticles (NPs) in biomedical and biological applications [1,2].
The interaction between NPs and proteins is known to induce several effects, such as promotion or inhibition of protein aggregation, adsorption of proteins at the NPs's surface or protein conformational changes [3-6].
When NPs are in contact with complex biological fluids, the surfaces progressively and selectively adsorb biomolecules, forming a biomolecular layer in close contact with the NPs: the "protein corona" [7-9]. It has been proposed that the biocorona determines the biologi¬cal interactions of NPs with the system where they are located, providing the biological identity of the materials [10].
The mechanism of interaction between NPs and proteins is still poorly understood [11-13]. In particular, the effects of NPs on the structural properties of proteins forming the protein corona are completely unknown.
In this work, the influence of different NPs on proteins structure is investigated by several biochemical and biophysical methods, including UV-Vis absorption, Fourier transform infrared (FTIR) and circular dichroism (CD). The evolution of the biocorona, as a function of critical parameters of the incubation conditions, has been monitored and characterized by these spectroscopic methods. The effects of protein-NP interactions on protein conformational properties have been evaluated and compared among different NP and protein types.

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Poster A25

INTERFACE ANALYSIS ON A FUZZY COMPLEX BY COMBINED ESI-IM-MS AND MODELING

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Intrinsically disordered proteins (IDPs) form biologically active complexes that can retain a high degree of conformational disorder, escaping structural characterization by conventional approaches. An example is offered by the complex between the intrinsically disordered NTAIL domain and the phosphoprotein X domain (PXD) from measles virus (MeV) that is crucial for MeV replication. While NTAIL is an intrinsically disordered domain of 125 residues, PXD (55 residues) is folded into an ordered threehelix bundle. Upon binding to PXD, NTAIL undergoes induced folding localized in an 18-residue α-helical region and this α-helical molecular recognition element (α-MoRE) associates to PXD forming a four-helix bundle.

We herein combine ESI-MS, ESI-IM-MS and computational methods to describe the NTAIL-PXD complex from MeV. The results of this study show that the MeV NTAIL–PXD complex is amenable to MS analysis and that distinct conformational states can be detected. While previous atomic models focused only on the α-MoRE region of NTAIL [2], this study combines experimental data and computational modeling to generate models at atomic resolution of the entire NTAIL–PXD complex, extending contact analysis also to the fuzzy regions of the complex which are likely involved in biological function. The resulting models indicate that interactions characterizing this molecular ensemble are mainly of hydrophobic nature although hydrogen bonding and electrostatic interactions seem to play a role in stabilizing the more compact states. The prevalently hydrophobic nature of the NTAIL–PXD complex is in agreement with previous reports highlighting that although IDPs are characterized by a low content in hydrophobic residues, not sufficient to drive formation of a hydrophobic core, hydrophobic residues often play a dominant role in mediating physiologically relevant protein-protein interactions.

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Poster A26

GREEN TYRE COMPOUNDS: AN INNOVATIVE APPROACH

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Tire is one of the most complex hybrid material containing different components, such as natural and/or synthetic rubber, antidegradants, curatives, processing aids and reinforcing fillers. SiO2 is commonly used to enhance the static and dynamic properties of rubber composites, which are significantly affected by the surface functionalization and by the size and shape of the filler nanoparticles [1]. Tuning these characteristics allows modulating the formation of a homogeneous and continuous percolative network within the rubber matrix, which represents a key point for providing effective reinforcement. Moreover, our group have recently demonstrated that the control of the particle morphology and alignment can provide a high percentage of immobilized rubber leading to a higher degree of reinforcement [2]. These results suggest that the use of anisotropic filler may be a promising approach for effectively improving the mechanical properties and for a potential reduction of silica filler in rubber compounding. With respect to this, the aim of this work is to study natural organoclay and in particular phyllosilicates, namely sepiolite and montmorillonite, as possible reinforcing fillers on the basis of their intrinsically anisotropic character. Due to both high surface area and aspect ratio, the addition of small amount of nanoclay could provide significant reinforcement and better mechanical properties, if it is well dispersed in rubber. The technique to convert this individually layered structure into a single silicate sheet in the polymer matrix will be investigated by exfoliation and intercalation approaches. The hydrophilic character of filler could be modified by grafting organic group and controlling surface free energy for improving the compatibility in rubber matrix. The properties of new rubber/clay nanocomposites will be evaluated on the basis of several aspects, including the type of intercalant, the melt-blending conditions, and the vulcanization process. The new nanocomposites will be characterized by complementary techniques such as X-ray diffraction (XRD), Fourier transformer infrared spectroscopy (FTIR), transmission electron microscopy (TEM), atomic force microscopy (AFM) and solid state NMR. In addition, the dynamic-mechanical analysis and tensile stress-strain tests will be performed to further investigate the influence of the anisotropic clay particles on the mechanical behavior of the nanocomposites.

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Poster A27

DESIGN AND CHARACTERIZATION OF PHOTO- AND THERMO-CROSSLINKABLE MATERIALS FOR PHOTOVOLATIC APPLICATIONS

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Organic π-conjugated materials are the core components of a large number of modern technologies having an increasing impact on everyday life. The development of performing materials for technological applications requires in the first place the capability to design molecules and/or polymers with suitable solution performances. Assembly of solid state devices also requires the capability to control the aggregation process while transferring the molecules/polymers from the solution to the solid state. The degree of control over the solid-state morphology is at least as important as the capability to control the molecular optoelectronic properties.
In this contribution we discuss our recent results in the development of photo- and thermo-crosslinkable conjugated materials[1] to be employed as donor and acceptors in organic photodiodes and solar cells. We will particularly focus on squaraine,[2] diketopyrrolopyrroles[3] and naphthalene diimide derivatives that are amongst the most performing materials so far described for OPV applications.

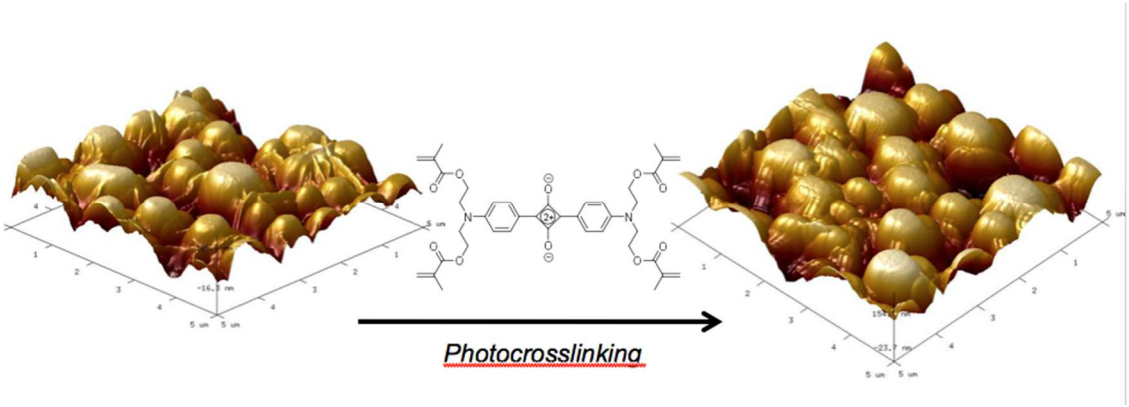

Figure 1. AFM images of pristine (left) and photocrosslinked (right) fullerene and acrylic squaraine mixture.

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Poster A28

POST-DEPOSITION ACTIVATION OF LATENT HYDROGENBONDING: A NEW PARADIGM FOR ENHANCING THE PERFORMANCES OF BULK HETEROJUNCTION SOLAR CELLS

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Small conjugated molecules (SM) are rapidly gaining momentum as a valid alternative to semiconducting polymers for the production of solution-processed bulk heterojunction (BHJ) solar cells, as they allow to overcome current limitations imposed by the intrinsic polydispersity of long conjugated chains and low batch-to-batch reproducibility. The major issue with SM-BHJ solar cells is the low carrier mobility due to the scarce control on the phase segregation process and consequent lack of preferential percolative pathways for free carriers to the extraction electrodes.
Here we demonstrate a new paradigm for fine tuning the phase segregation in SM-BHJs based on the post-deposition exploitation of latent hydrogen bonding in binary blends of functionalized electron-donor moieties mixed with PCBM. The key aspect of the approach, schematically depicted in Fig. 1a, is the temporary 'deactivation' of the H-bond-forming sites of the donor molecule by its protection with a thermally labile functionality. This makes the donor miscible with PCBM in common solvents, allowing for the use of conventional solution-based deposition methods on transparent conductive substrates. The formation of phase segregated domains is successively finely tuned by thermal cleavage of the protective group and consequent activation of the H-bonding sites. Through this approach, we can control the blend morphology from the initial kinetic structures formed during film deposition (i.e. evaporation of the solvent during spin-coating) all the way to thermodynamic macrophase-separated materials and thereby access intermediate morphologies that simultaneously optimize the charge separation efficiency at the donor/acceptor interfaces and charge mobility through the formation of interpenetrated phase separated percolation pathways. As a result, the PV efficiency undergoes an over twenty-fold increase with respect to control devices. This strategy, demonstrated here with a binary mixture of diketopyrrolopyrrole derivatives (Fig.1b) with PCBM, can in principle be extended to other molecular systems for achieving highly efficient, stable, small-molecule BHJ solar cells.

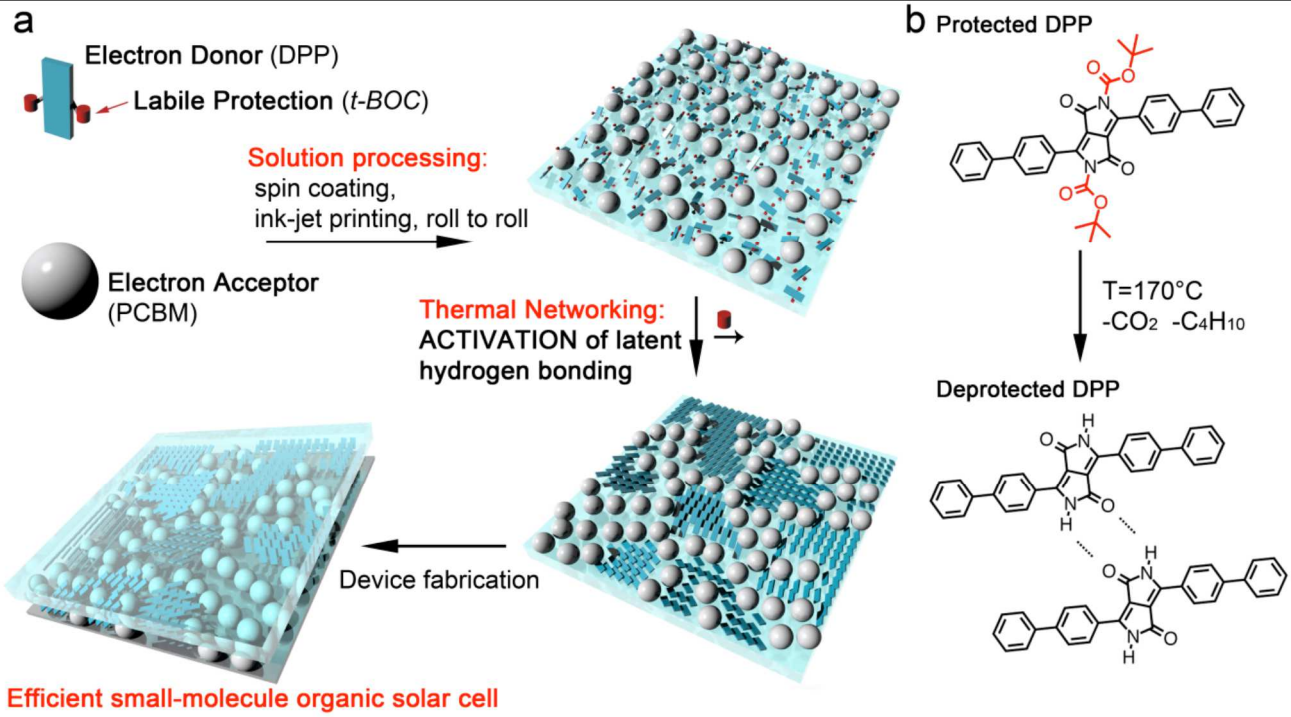

Figure.1 Concept of latent H-Bonding activated phase segregation in SM-BHJs. a) Schematic representation of the latent H-bonding strategy in the fabrication of SM-BHJ solar cells. A solution of protected donor and acceptor molecules are deposited on transparent conductive substrates via simple solution processing (i.e. spin coating, roll-to-roll printing). The post-deposition thermal treatment removes the thermolabile protective functionalities thereby activating the latent H-bonding sites. As a result, the donor moieties network leading to a fine controlled phase segregated polycrystalline film. Deposition of the extraction electrodes is carried out by standard procedures. b) Activation of latent H-bonding in *di-tert-butyl3,6-di([1,1'-biphenyl]-4-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate*. At 170°C the ter-butoxycarbonyl (t-BOC) protection group (highlighted in red) is converted in *carbon dioxide* (CO_2) and *isobutene* (C_4H_{10}).

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Poster A29

THE EFFECTS OF EMBEDDED DIPOLES IN AROMATIC SELF-ASSEMBLED MONOLAYERS

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We describe a novel approach for changing the work functions of self-assembled monolayers (SAMs). Replacing the middle phenylring of terphenylmethanethiol by the polar pyrimidine ring results in an embedded dipole moment, which can either point towards or away from the docking group/gold surface, depending on the orientation of the pyrimidine ring. Similar effects have been achieved via tail-group substitution at the SAM-forming molecules, what has several drawbacks, because the SAM-ambient interface is highly affected.[1] Without modifying the SAM-ambient interface our SAMs allow for tuning the substrate work-function significantly, as illustrated by Kelvin probe measurements and ultraviolet photoemission spectra. High-resolution X-ray photoelectron spectroscopy in combination with a quantum-mechanical description of the interface properties also shows that the embedded dipoles enable manipulating the electrostatic potential locally within the SAM. Complementary surface techniques, (ellipsometry, infrared reflection absorption spectroscopy (IRRAS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and scanning tunneling microscopy) are used to ensure film quality and comparability, and thus, the reliability of our conclusions.

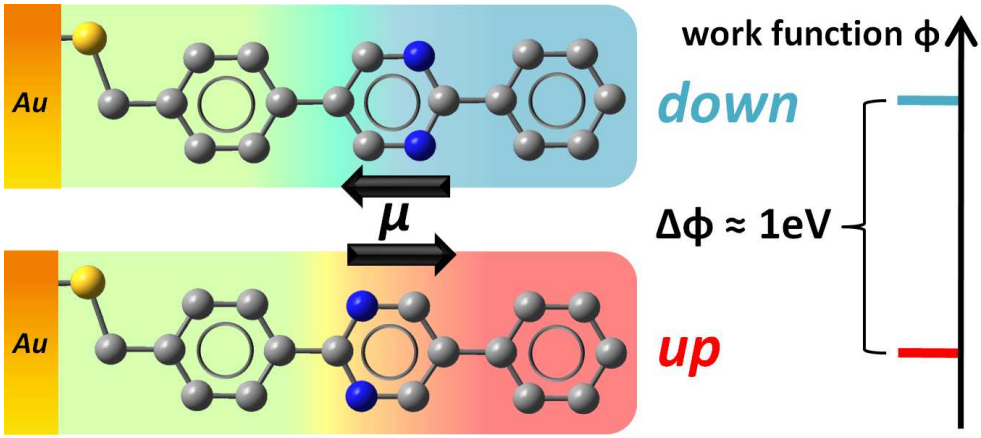

Figure 1. Embedded dipoles in mid-chain substituted aromatic SAMs for work function tuning.

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Poster B1

POLYCRYSTALLINE-GOLD/LIQUID INTERFACES: FUNCTIONALIZATION TECHNIQUES FOR BIO-SENSING AND DIGITAL MICROFLUIDICS

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Interactions between liquids and solids are deeply influenced at nano- and micro-scale by solid surface characteristics and properties (morphologic, chemical or electrical properties). Surface functionalization techniques allow us to tune intrinsic properties or to give completely brand new ones to almost every kind of surface or material. In this work are shown two different kinds of surface functionalization for Bio-sensing in liquid or electrowetting on polycrystalline Au.

Organic electronic devices can be fabricated on flexible, biocompatible even biodegradable substrates [1] and can work in liquid environment. For all these reasons Organic Field-Effect Transistor (OFET) are emerging devices in biosensing. Kergoat et al. [2] demonstrated in 2010 that OFET operated into an electrolyte, so called EGOFET, is stable, and since then, EGOFET was demonstrated to detect DNA, neurotransmitters, pH changes and dopamine [3].

In this work, EGOFET in the traditional configuration is enclosed in a PDMS □-fluidic system (Fig.1). In our EGOFET the Au gate electrode in the electrolytic solution is functionalized with a bio-recognition moiety. When target molecules are present in solution, they bind at the gate electrode and cause a change in the potential at the electrode. Even very small changes of the Gate potential (few bindings events) affect electrostatic potential at the solution/organic semiconductor interface, because this interface is coupled to the semiconductor channel by the very large capacitance of the Debye-Helmholtz layer.

Self-assembled monolayer (SAMs) are a versatile tool for modifying surface properties of metals, semi-conductors and insulators [4]. SAMs can be used successfully for several purposes, such as corrosion inhibition, lubrication and wettability. Wettability is tuned by the electrostatic effect caused by charging of the electrostatic double layer at the dielectric/solution interface. Sondag-Huethorst et al. [5] demonstrated that wettability can be controlled by introducing redox processes in the interface between surface and liquid. In our system we used non commercial olygoarylene thiols (4-nitro-terphenyl-4”-methanethiol NTM and 4-nitro-terphenyl-3”,5”-dimethanethiol NTD) self-assembled on Au [6,7]. We exploited the presence of the electroactive nitro (-NO2) group to tune wettability of the surface applying low potential. We first studied electrochemistry to shed light on the mechanism of the redox processes occurring at the surface, then monitored changes in the surface tension by exploiting the redox chemistry of the -NO2 group, finally demonstrated the potential use of such SAM-forming molecules for electro-wettability applications. Digital μ-fluidics and surfaces characterized by tunable wettability can be used in interfaces between metal/organic surfaces and bio-world; they allow to modify locally the physical-chemical properties of a surfaces when needed.

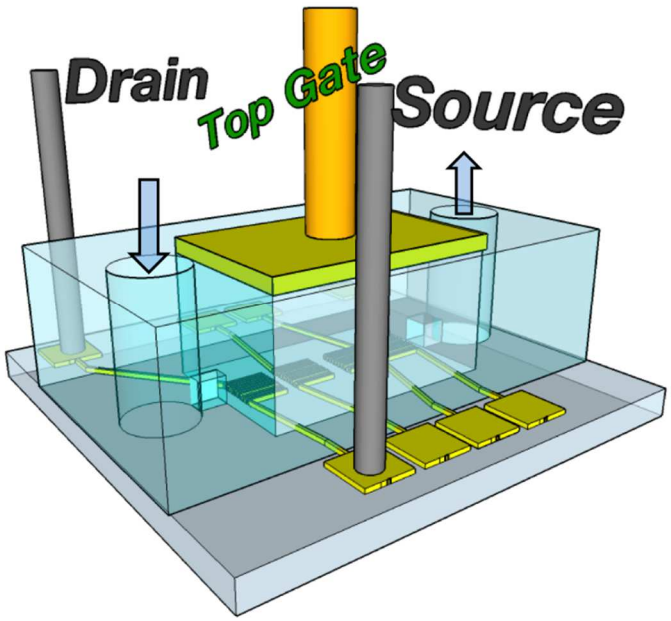

Figure 1: Schematic cartoon of our EGOFET coupled with a □-fluidic system

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Poster B2

UNDERSTANDING THE PH-DEPENDENCE OF A PENTACENE-BASED ELECTROLYTE-GATED ORGANIC FIELD-EFFECT TRANSISTOR (EGOFET)

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Organic Thin-Film Transistors were demonstrated to be stable in liquid environment in 2010 [1]. One of the possible layout (EGOFET) is shown in Fig.1. In this architecture, the gate dielectric is constituted by a small amount of electrolytic solution yielding an higher capacitive coupling with respect to the conventional dielectrics (i.e. from nF/cm2 to μF/cm2) and lower operational voltages (<-1V). The organic semiconductor is directly exposed to the aqueous solution, which guarantees high sensitivity to small changes at both interfaces: (i) electrolyte/gate and (ii) organic semiconductor/electrolyte.

EGOFETs are extremely versatile, in fact biocompatible and biodegradable materials are being implemented for their fabrication, aiming at implantable devices.

Within this context, pH monitoring is an ideal benchmark to test the EGOFET sensitivity. Local changes of pH are involved in several biological events, such as catalysis, inflammation, anomalous metabolic activity, etc. So far, pH-meters based on Ion Sensitive Field Effect Transistors (ISFETs)[2], Dual-Gate Organic Field Effect Transistors [3] and EGOFETs [4] have been successfully reported.

Here a pH-meter has been developed, exploiting an unconventional fabrication technique [5]. The whole layout has been firstly drawn thanks to a Computer Aided Drafting (CAD) software and then transferred on a golden quartz slide (featuring a thin-film of Ti 2nM thick and Au 40 nm thick) by means of laser ablation.

A Pt wire acts as the gate electrode, which is immersed in the electrolyte confined by a polypropylene pool sealed onto the active area of the electronic device. A pentacene thin-film (nominal thickness of 15 nm, namely 10 monolayers [6]) is sublimed by ultra-high vacuum deposition. Phosphate buffer (100 mM in H2O) is the gate "dielectric", whose pH has been set adding HCl or NaOH solutions.

Our EGOFET turns out to be sensitive for both basic (from 7 to 11) and acidic (from 7 to 1) environment. The threshold voltage (V_{th}) and the source-drain current (I_{DS}) show pH-dependent behavior. In particular, the V_{th} sensitivity is equal to 36 mV/pH at acidic pH, whereas is 25mV/pH at alkaline one. This means a negative V_{th} shift along with a IDS decrease, which is coherent with the site-binding model [7] combined with Gouy-Chapman-Stern one [8]. At acidic pH, silanol protonation occurs on quartz substrate, thus the accumulation of positive non-mobile charges depletes the p-type channel. At alkaline pH, the ionic strength of the electrolyte increases, giving rise to higher electrostatic screening, which induces a weakening of the capacitive coupling between gate electrode and organic semiconductor. This means less available charges within the conductive channel.

Finally, our device turns out to be sensitive in the whole range of pH (from 11 to 1) featuring a reversible and stable behavior. The mechanical compliance together with the extreme versatility makes our EGOFET appealing to a wide range of applications in different fields such as bio-sensing, food monitoring and diagnostics.

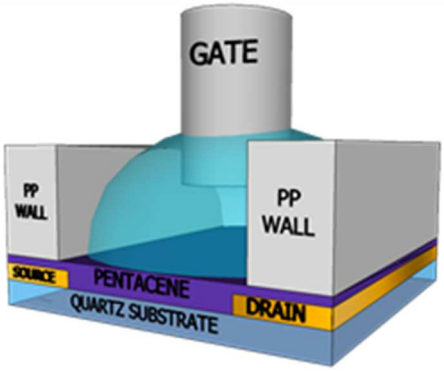

Figure 1. Functional cartoon of the EGOFET device

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[8] A. Härtl, J. A. Garrido, S. Nowy et al., *J. Am. Chem. Soc.* **129** 1287 (2007)

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Poster B3

TOWARDS SPATIALLY RESOLVING PHOTOELECTROCHEMICAL SENSORS

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Sensing devices for biological molecular species such as proteins or sugars in solution are receiving increasing interest. They enable monitoring of physiological parameters or can lead to bioelectronics. We are aiming on multi-analyte systems which are based on a spatially resolved optical excitation of functionalized quantum dot arrays. It requires specific and reproducible spatial arrangement of nanoparticles and an efficient coupling to the sensor electrode to enable charge transfer. Therefore, self-assembling monolayers (SAMs) were introduced as linker layers.
As a first step, we developed tools and strategies to achieve patterns of different nanoparticles. By means of microcontact printing (μCP) an array of alternating methyl- and hydroxyl-terminated molecule regions was fabricated. Hence forming SAMs of hydrophobic and hydrophilic character, the layer serves as template for selective assembly of respectively coated nanoparticles. Optical and fluorescence micrographs reveal the microstructure of juxtaposed regions of nanoparticles exhibiting different photoelectric character. Furthermore, AFM operated in height- and friction-sensitive mode serves as means to image patterns on small scale.
Addressing an effective and stable coupling of quantum dots an aromatic dithiol was implemented. As shown previously, SAMs of 4,4'-dimercaptostilbene provide a suitable linker that combines structural order and sufficient conductance [1]. We investigated the ordering, quality and thermal stability on Au(111) surfaces by means of XPS, NEXAFS and TDS and showed a critical dependence on preparation parameters, such as the assembling temperature and choice of solvent.

[1] W. Khalid et al., *ACS Nano* **5** 9870 (2011).

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Poster B4

THERMOELECTRIC CHARACTERIZATION OF DOPED ORGANIC LAYERS

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The performance of organic opto-electronic devices such as organic solar cells and organic light emitting diodes can be significantly improved by the introduction of p- and n-doped transport layers into the device architecture. In this way, the charge carrier extraction or injection from or into the organic photo-active layer is improved and ohmic losses are reduced. Molecular doping of organic host materials increases the conductivity of a transport layer and moves the Fermi level to the appropriate position to work as electron or hole selective transport layer. In this work, we use Seebeck effect and temperature-dependent conductivity measurements in order to determine the dominating type of charge carriers introduced by the dopant and gain insight to the position of the transport level with respect to the Fermi level. The investigation of fullerene dopants with a different degree of fluorination allows us to tune the energy level offsets between host and dopant and study their influence on the Fermi level position and overall doping efficiency systematically. The results give further insight to the underlying principles of molecular doping, necessary for understanding and improving organic opto-electronic device performance.

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Poster B5

SIMPLE STRUCTURING & EXCELLENT PERFORAMCE
AN UPCOMING ORGANIC PERMEABLE-BASE TRANSISTOR

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With the goal of high-frequency operation, vertical organic transistors provide low-cost fabrication techniques for realizing short channels in the sub-micrometer range - simply determined by the chosen semiconductor thickness. We present an organic permeable-base transistor (OPBT) with a 'sandwich'-like geometry as known from OLEDs, structured by thermal vapor deposition and low-cost shadow masks. The OPBT-stack (Fig. 1a) consists of an insulated, grid-like base electrode (B) [1] in the middle which is embedded in two C_{60} layers and two outer electrodes: emitter (E) and collector (C). We realize downscaled transistors with an active area of (200 µm)² by integrating an insulating layer (turquoise). With a low subthreshold slope of 100 mV/decade, the devices reach current densities of 10 A/cm² and an on/off ratio greater than 10^6 at a low driving voltage of 1.0 V (Fig. 1b). A transit frequency of 2.2 MHz is measured with an optimized measuring setup [2]. With these results, our OPBTs reach higher performance than devices built using similar low-cost structuring techniques and can keep up even with OTFTs exhibiting higher charge carrier mobilities or devices using high resolution structuring [3].

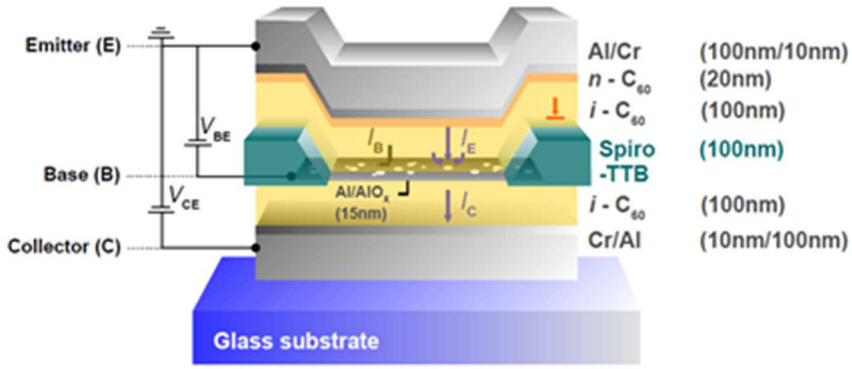

Fig 1: (a) Cross section of the presented C_{60}-OPBT. The 'sandwich' architecture consists of an insulated, nano-porous base electrode in the middle which is embedded in to C_{60} layers and two outer electrodes. The vertical current is controlled by the base potential.

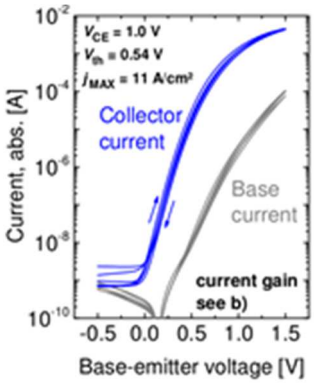

Fig 1: (b) The base sweep measurement. An on-state current density of 10 A/cm² and an on/off ratio greater than 10^6 is achieved at a low operation voltage of 1 V.

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[2] B. Kheradmand-Boroujeni et al. *IEEE Trans. El. Dev.* **61**(5), 1423-1430 (2014);
[3] M. P. Klinger, A. Fischer, F. Kaschura et al. submitted to *Adv. Mater.* (2015)

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Poster B6

VAPOR-DEPOSITED AMORPHOUS ORGANIC THIN FILMS WITH ENHANCED THERMAL STABILITY FOR OLED DEVICES

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Glasses, by nature, are homogeneous, isotropic and free from phase/grain boundaries or crystalline defects, properties that make them more suitable than the crystalline phase when prepared over large areas or flexible substrates. However, glasses are inherently unstable and can evolve over time leading to changes in their properties. Vapor deposition has recently emerged as a new methodology for preparing glasses with extraordinary stability[1], dubbed ultrastable glasses, which show a promising potential in the improvement of state-of-the-art organic light-emitting devices (OLEDs). Higher thermal and kinetic stabilities, higher carrier mobilities[2], preferential molecular packing[3] and higher density are some of the enhanced properties that can be achieved by tuning the deposition conditions. The characterization of the glass transition gives access to the kinetic and thermodynamic properties of the glass. Differential scanning calorimetry and, specifically, membrane-based fast-scanning (10^4-10^5 K/s) nanocalorimetry have proved their suitability[4] for characterizing thin and ultrathin glassy films. These techniques allow the measurement of the glass transition onset, the transformation rate and the enthalpy excess. Here we present preliminary results about the thermal stability of ultrastable thin films made of an organic molecule with potential interest for OLED devices.

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[4] Leon-Gutierrez, E., et al. *The Journal of Chemical Physics* **129**.181101 (2008)

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Poster B7

PEROVSKITE PIGMENTED SOLAR CELLS WITH NOVEL HOLE TRANSPORTING LAYER TO IMPROVE EFFICIENCY AND STABILITY

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Recently, hybrid organo-lead perovskite based solar cells have shown the best performance in solid state based hybrid solar cells. The Hole Transporting Layer in organolead halide perovskite solar cell represents one of the key components to achieve high power conversion efficiency (PCE). Currently, for best performing solid state devices, doped Spiro-OMeTAD (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl amine)-9,9-spirobifluorene) have been used as a hole transport material (HTM) for transporting holes from perovskite to the counter metal electrode. However, Spiro-OMeTAD cannot be used as such for the fabrication of efficient devices. It requires p-doping to increase its conductivity by the addition of Lithium bis(trifluoromethane)sulfonimide salt (LiTFSI) and 4-tert butylpyridine (t-BP) additive. The doping improves its performance but simultaneously decreases its stability and consider as bottleneck. To overcome this pressing issue, we have used hydrophobic dopant as an additive in Spiro-OMeTAD and other HTMs. The addition of such dopant improves the solar cell stablility significantly.
Furthermore, to replace the high expensive Spiro-OMeTAD as HTM, a series of low cost, facile synthesized new small organic molecules based on a highly conjugated core and triarylamine moieties were also prepared and integrated in devices. The HOMO-LUMO energy levels were tuned by incorporating methoxy group on the triarylamine moiety and optical, electrochemical properties of these novel molecules were studied by optical absorption spectrophotometry, fluorescence spectrophotometer and cyclic voltammetry measurements.

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Poster B8

HUMIDITY EFFECTS AT THE ORGANIC/POROUS SILICON SENSOR INTERFACE

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Biosensing technology is a rapidly advancing field that benefits from the possibility to use the properties of functional advanced materials to analyse biological systems. In particular, nanomechanical systems are very attractive for biological sensing since mechanical interactions are fundamental to biology. Indeed, nanomechanical devices allow measuring forces, displacements and mass changes from cellular processes, and provide high sensitivity and fast responses, which is necessary for the observation of biological processes [1]. On the other hand, among all the functional materials, PSi constitutes an ideal substrate for developing new chemistries owing to its biocompatibility, well-established fabrication methods and large adsorption surface, which allows an enhanced sensitivity [2]. In this work, we will start by reviewing the processes for the PSi formation on microcantilevers and their biofunctionalization in order to trigger its sensitivity as biosensing platform. Secondly, we will describe current approaches based upon modification by self-assembled silane monolayers, which critically depend on the type of process for the activation of PSi. Depending on the molecular structure of the monolayers, the surface will present hydrophobic/hydrophilic properties, will allow a molecular selectivity, and a local control of the biomolecular interactions. The surface of the functionalized material will then be biologically activated for the detection of specific genomic or proteomic species applying surface immobilization techniques. Finally, the process of formation of the biorecognition interface will be applied to composite porous silicon-crystalline silicon cantilevers and preliminary results will be shown.

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Poster B9

STUDY OF LIGHT ABSORPTION ENHANCEMENT BY NANO- AND MICRO -STRUCTURES IN ORGANIC SOLAR CELLS

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The organic bulk hetero-junction solar cell has remarkable advantages such as low cost, mechanical flexibility and simple process techniques. Recently, low-band gap photoactive materials have obtained a significant attention due to their potential to absorb a wider range of the solar spectrum to attain higher power conversion efficiencies. Many low-band gap photoactive materials, however, still show a relatively low external quantum efficiency of less than 60% [1]. One possible approach to improve the device performance is to increase the light absorption in the active layer. This may, among other approaches, be achieved by using nano- or micro-structures that trap light at specific wavelengths [2], or by using the localized surface plasmon resonance effect of metal nanoparticles in the devices. In this work, we theoretically study various plasmonic materials and structures, based on finite-difference time-domain numerical modeling, in order to optimize their effect in the organic solar cells. With aid of the developed numerical model, we optimize the plasmonic structures in developed devices for obtaining higher efficiencies.

[1] S.-W. Baek, G. Park, J. Noh, C. Cho, C.-H. Lee, M.-K. Seo, et al *ACS Nano* **8** 3302-3312 (2014)
[2] R. M. d. O. Hansen, Y. Liu, M. Madsen, and H.-G. Rubahn, *Nanotechnology* **24** 145301 (2013).

‡ Mirsafaei@mci.sdu.dk

Poster B10

UP-SCALING OF INVERTED SMALL MOLECULE BASED ORGANIC SOLAR CELLS

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Organic solar cells (OSC), in spite of being a promising technology, still face challenges regarding large-scale fabrication. Although efficiencies of up to 12 % has been reached for small molecule OSC, their performance, both in terms of device efficiency and stability, is significantly reduced during up-scaling processes. The work presented here is focused on an approach towards up-scaling of small molecule based OSC with inverted device configuration. Bilayer OSC from Tetraphenyldibenzoperiflanthene (DBP) and Fullerenes (C_{70}), as electron donor and acceptor respectively, with cell area ranging on a scale from a few mm^2 to cm^2, are produced by organic molecular beam deposition (OMBD). All the layers in the device are fabricated from a highly sophisticated vacuum cluster deposition system that includes electrode, interfacial layer and organic layer deposition in one high-vacuum deposition system. The work includes investigation of morphology and uniformity of the layers from atomic force microscopy (AFM) and optical spectroscopy investigations.

Poster B11

ELECTROLUMINESCENCE FROM CHARGE-TRANSFER STATE IN ORGANIC SOLAR CELLS

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Charge photocurrent generation is a key process in solar energy conversion systems. Effective dissociation of the photo-generated electron-hole pairs (excitons) has a strong influence on the efficiency of the organic solar cells. Charge dissociation takes place at the donor/acceptor interface via charge transfer (CT) excitons, which is Coulombically bound interfacial electron-hole pairs residing at the donor/acceptor heterojunctions. The CT state represents an intermediate state between the exciton dissociation and recombination back to the ground state. Since the recombination of photo-generated charges is a major limitation for the efficiency of the organic solar cells, a thorough understanding of this loss mechanism is crucial to improve the performance of the devices. Furthermore, examining this interfacial state is of great importance in order to maximize open-circuit voltage and photocurrent simultaneously as they both depend on it[1]. As a useful method, Electroluminescence (EL) measurements can be applied to examine CT-state emission. In this method[2], CT states are created by injection of electrons and holes into the device, and the luminescence originated from free carrier recombination at the donor/acceptor interface is detected. As a less studied system, we examine here the interfacial charge transfer state recombination in DBP:C_{70} thin-films. The weak EL from the small molecule solar cell biased in the forward direction gives valuable information about the CT state recombination, from which the maximum open-circuit voltage can be estimated, and further can be used in the modeling and optimization of the OPV devices.

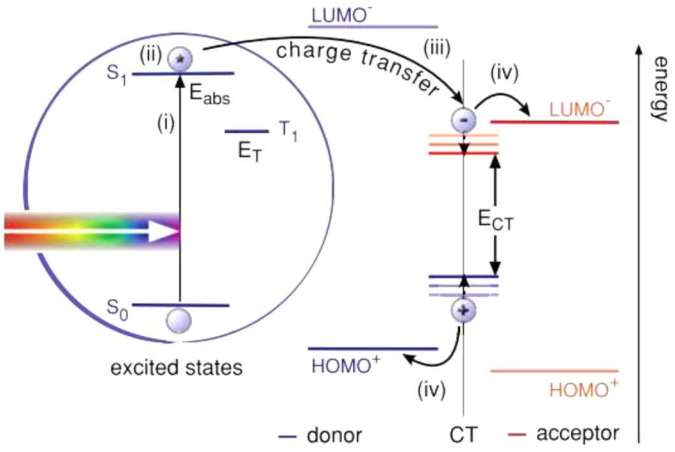

Figure 1. Energy level diagram of a donor-acceptor interface showing the CT states that present the intermediate state between the exciton dissociation and recombination[1].

[1] C. Deibe, T. Strobe, and V. Dyakonov, *Adv. Mater.* **22** 4097–4111 (2010).
[2] K. Tvingstedt, K. Vandewal, A. Gadisa, F. Zhang, J. Manca, and O. Inganäs, *J. Am. Chem. Soc.***131** 11819–11824 (2009).

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Poster B12

A STEP TOWARDS STABLE SMALL MOLECULE ORGANIC SOLAR CELL

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In order to achieve Organic Solar Cell with high performance, both in terms of high efficiency and stability, there is a need to investigate the properties of each layer from different characterization methods; In order to optimize device performance, we here investigate the crystallinity, morphology, molecular orientation as well as Exciton diffusion length and lifetime of the employed organic layers. The characterization methods that will be used include XRD, variable angle spectroscopic ellipsometry (VASE), AFM, as well as femto-second optical spectroscopy. To tune the morphology and molecular orientation in the devices, we here investigate the effect of elevated substrate temperatures and substrate composition during thin-film growth, and optimize the films for use in high performance organic solar cells. The obtained high performance devices will set the base for investigating degradation mechanisms and optimize the devices towards long-term stability.

Poster B13

ARCHITECTURE-SPECIFIC CONTRIBUTIONS TO SHORT CHANNEL EFFECTS IN ORGANIC TRANSISTORS

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Organic thin film transistors still suffer from an insufficient stability and cannot compete with the performance of their inorganic counterparts. Nevertheless, highly promising advances in switching speeds were achieved upon aggressive scaling of device dimensions such as the channel length and the gate dielectric thickness [1, 2]. The benefits of reducing the channel length, i.e., the separation of source and drain are, however, counteracted by non-desired short channel effects and increasingly dominant contact resistances. Moreover, theoretical work indicates that, in general, the contact resistance is strongly related to the efficiency of injection at the contacts and depends not only on the carrier mobilities and injection barriers, but also on the device dimensions, the device architecture, and the point of operation. [3, 4]

We, therefore, investigate the dependence of the contact resistance on the abovementioned properties for channel lengths varying by 4 order of magnitudes, i.e., from several micrometers to 100 nanometers and below. We utilize two-dimensional drift-diffusion-based simulations including the self-consistent consideration of thermionic and tunneling injection, interface recombination, and back drift, to determine the contact resistance and short channel effects directly from the simulation of the device at a given point of operation. We particularly focus on how the onset and the extent of short channel effects for given material properties depend on the actual device architecture, i.e., the staggered (top-contact bottom gate) or the coplanar (bottom-contact bottom-gate) device configuration.

We demonstrate that conventional methods to extract the contact resistance, i.e., the transfer line method, fail for both architectures due to a profound dependence of the contact resistance on the channel length.[5] Based on our analysis of the relationships between material and geometric parameters, we suggest architecture-specific routes to suppress short channel effects.

[1] F. Ante, D. Kälblein et.al., *Small* **7-9** 1186-1191 (2011)
[2] H. Kleemann, A. A. Günther et.al., *Small* **9-21** 3670-3677 (2013)
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[4] F. Maddalena, M. Spijkman et. al., *Org. Electron.* **9-5** 839-846 (2009)
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Poster B14

ELECTRICAL IN-SITU CHARACTERISATION OF ORGANIC THIN FILM TRANSISTORS

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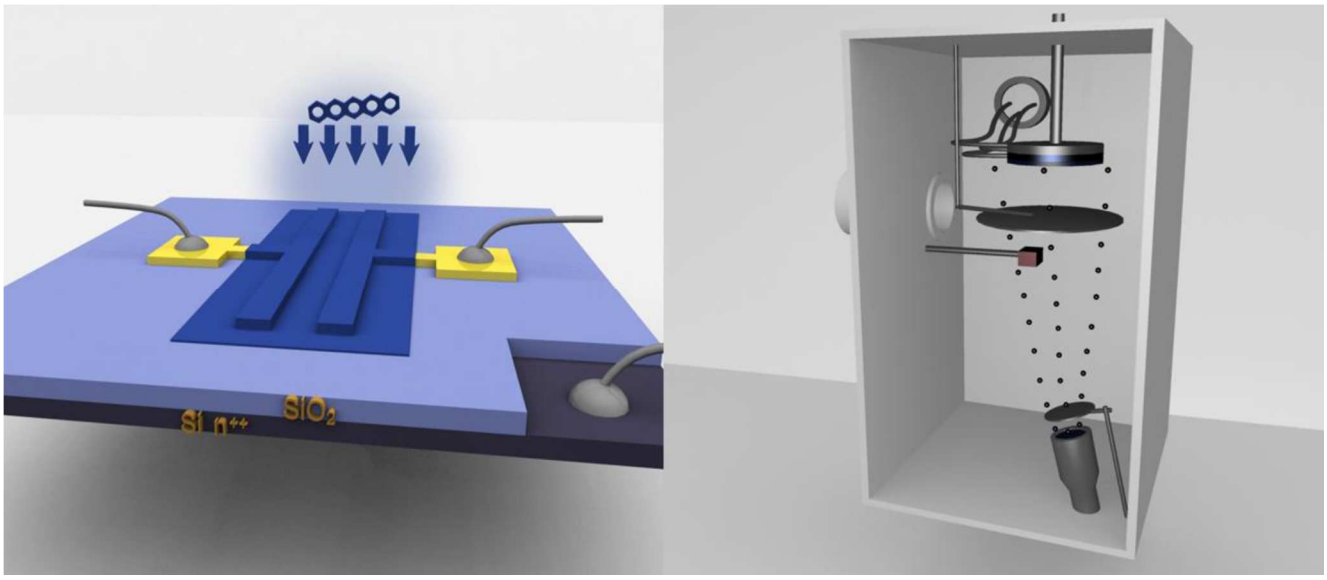
In the present contribution we report on the electrical in-situ characterisation of p- and n-type type OTFTs in bottom gate – bottom contact (coplanar) geometry on highly doped <100> Si-substrates. A 150 nm thick layer of thermal silicon oxide with an optional polymer interface passivation layer serves as the gate dielectric whereas pentacene (p-type) and C_{60} (n-type) are chosen as organic semiconductor (OSC). The OSC is evaporated on pre-fabricated model device structures by organic molecular beam epitaxy in a high vacuum system adapted to enable parallel in-situ electrical characterisation during the ultra-slow deposition of the semiconductor film. Thus, the experimental setup allows for the observation and analysis of the dynamics of channel formation and the dependence of electrical device characteristics on the thickness and morphology of the OSC-layer, which in turn reveal information about the OSC/dielectric-interface. Charge transport within the devices is investigated in direct correlation to the number of monolayers deposited. The evolution of transistor parameters is studied both on SiO_2 and on bi-layer dielectrics. As bi-layer systems SiO_2 / poly((±)endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, diphenylester (PNDPE) is used for p-type-, and SiO_2/trimethylsilyl cellulose (TMSC) for n-type transistors, and compared to the behaviour on a pure SiO_2 dielectric.



Sketch of the model transistors in bottom gate-, bottom source/drain- (coplanar) configuration used in the in-situ measurements (left), and the experimental setup (right).

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Poster B15

NATURAL SOURCE BASED MATERIALS AS FUNCTIONAL LAYERS IN ORGANIC COMPLEMENTARY INVERTERS

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With the pervasive spread of electronic consumer products, penetrating every aspect of human`s lives, and the ever-growing need to keep these devices up to date, a huge amount of electronic waste is generated. Our responsibility for future generations demands electronics utilizing nature-based and biodegradable materials, thus paving the way towards green electronics. Adopting this approach the usage of cellulose is reported as a natural, biodegradable gate dielectric material that can be fabricated as an ultrathin high-k insulating film for low-voltage organic complementary inverters [1]. These inverters exhibit exceptional performance with respect to gain, noise margin and rail-to-rail output swing, strongly recommending cellulose films for green electronics. The device structure of the integrated OTFTs is displayed in Fig. 1. Additionally, the usage of a cellulose-derivate (trimethylsilyl cellulose, TMSC) as and ultrathin gate dielectric in low-voltage organic complementary inverters is reported [2]. These inverters outperform any inverter reported so far with respect to the combination of excellent key parameters such as a record DC gain well above 500 V/V (up to 1600 V/V), a low operation voltage level around 4 V, long term stability (45 days) and a record noise margin of 92.5%. In order to clarify the origin of this high performance, special attention was given to the investigation of the semiconductor-dielectric interface, the semiconductor morphology, the nature of traps, the influence of mobility levels on the inverter performance and long-term stability.

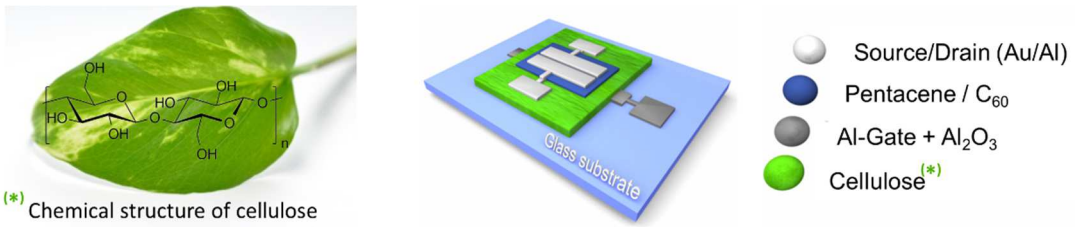

Figure 1. Schematic image of cellulose based organic thin film transistors

[1] A. Petritz, A. Wolfberger, A. Fian, A. Irima-Vladu, M. Haase, A. Gold, H. Rothländer, T. Griesser, T. Stadlober, B. *Appl. Phy. Lett.* **103** 153303-153307 (2013).
[2] A. Petritz, A. Wolfberger, A. Fian, T. Griesser, M. Irimia-Vladu, Barbara Stadlober, *Adv. Mat.* accepted.

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Poster B16

TEMPERATURE AND SURFACE MODIFICATION DEPENDENT ULTRA-HIGH VACUUM PENTACENE GROWTH:
IN-SITU TRANSISTOR FABRICATION AND CHARACTERIZATION

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Many of the underlying principles affecting critical organic field effect transistor (OFET) parameters, such as performance and lifetime, are not fully understood to the present date. We present analysis on the formation, structure and stability of the semiconducting layer in pentacene OFETs through a unique combination of in-situ layer deposition, real-time electrical and surface analytical characterization, all available during and subsequent to the deposition process itself. The investigations have been performed under ultra-high vacuum conditions, at temperatures ranging from 125 K up to semiconductor desorption. In-situ Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS) were performed parallel to the electrical investigations. Ex-situ atomic force microscopy allowed direct connections to be made between the temperature induced growth mode, morphology and charge transport mechanisms. Of special interest was the onset of the OTFT functionality as a function of layer thickness in combination with sample pretreatment [1]. In addition the evaluation of coverage and growth temperature dependent charge carrier mobilities proved to be of great interest in regard to contact resistance assessments. Newest results show, that a combination of layers grown at 350 K and 200 K outperforms films of the same total thickness deposited at only one sample temperature by an order of magnitude when it comes to the maximum attainable charge carrier mobility.

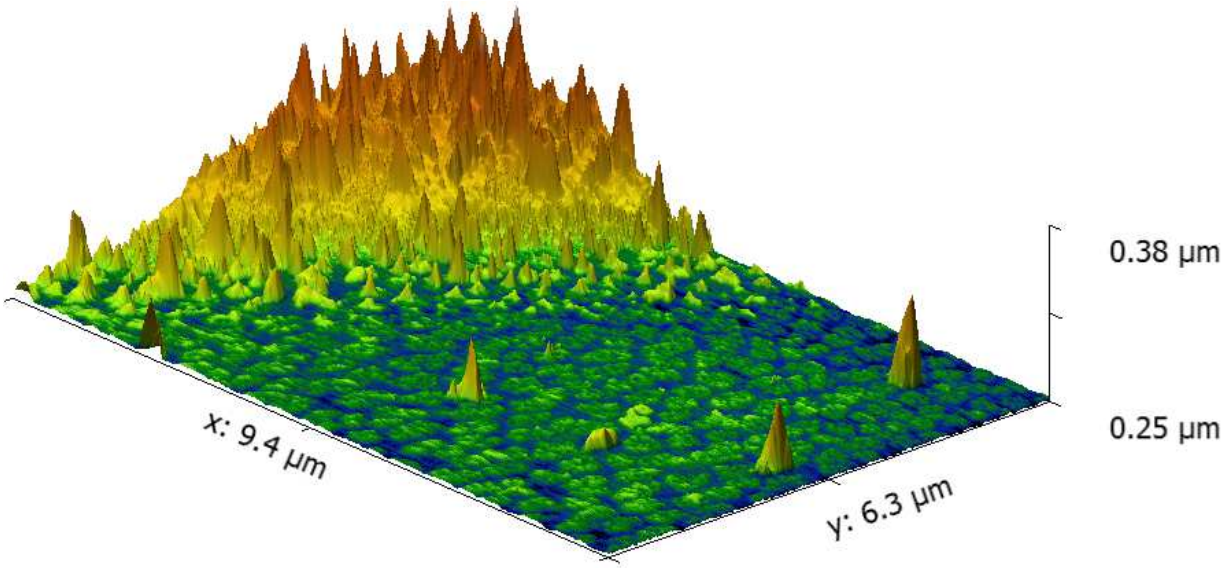

Figure 1. AFM picture of the silicon oxide channel (front) to gold contact (back) transition in a pentacene organic thin film transistor. Nominal pentacene coverage is 75% of one full monolayer.

[1] R. Lassnig, B. Striedinger, M. Hollerer, A. Fian, B. Stadlober and A. Winkler, *J. Appl. Phys.* **116** 114508 (2014).

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Poster B17

IMAGING NANOPLASMONICS (INPXTM), A MULTIFUNCTIONAL TECHNOLOGY PLATFORM

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Surface plasmon resonance (SPR)-devices are widely applied as biosensing platfoms allowing a rapid, real time, label free and multiplexed detection. However, the performance of the technology is often challenged by high instrumentation costs, poor interfacing capabilities with other analytical technologies and a lack of sensitivity when applied to direct detection of highly dilute targets or analytes with small molecular weight [1]. In order to overcome these challenges, extensive research has addressed the development of enhanced SPR platforms based on innovative nanomaterials and fabrication methods enabling low cost production of large area nanostructured surfaces and affordable miniaturized devices [2]. In addition, enhanced SPR active materials can be coupled to other analytical techniques, such as Surface Enhanced Raman Spectroscopy (SERS), fluorescence and MALDI-TOF MS, yielding a single biochip surface at the center of multiple orthogonal detection technologies and creating a sensor of improved capacity [3].
In this work, we describe a high performance plasmonic platform, based on the Imaging Nanoplasmonics technology (iNPx^{TM}). The sensor surface consists of a giga-array of gold/polymer nanopillars, acting as plasmonic enhanced nanoantennas and probed by an integrated and miniaturized optical setup. By playing with the geometrical features of the iNPx^{TM} nanoantennas, it is possible to tune the spectral position of the optical response; moreover, the simultaneous presence of localized and delocalized plasmonic modes allows the detection on two different sensitivity scale and paves the applicability for tracing small molecules. These surfaces have been proved to work as efficient platform for diagnostics, allowing a fast, real time and multiplexed sensing of proteomic biomarkers [4]. A proof of concept of the compatibility of iNPx^{TM} sensors with both SERS [5] and MALDI-TOF MS has been demonstrated and further developments are ongoing in the framework of THINFACE project.

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Poster B18

SUPER-SENSITIZED PHOTON UP-CONVERSION AT SUBSOLAR IRRADIANCE IN MULTICOMPONENT ORGANIC SYSTEMS

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The partial coverage of the solar spectrum strongly limits the solar cells (SC) efficiency. Sub-bandgap photons can be recovered by coupling to the SC an upconverting (UC) material to shift their energy to higher values [1]. Classical nonlinear UC, as well as UC in rare-earth based materials, requires high excitation densities (MW cm^{-2}) resulting unsuitable for solar applications. To the contrary, sensitized upconversion (sTTA-UC) in organic systems shows quantum yields up to 30% at irradiances of few suns (mW cm^{-2}) [2]. In sTTA-UC, converted light is generated through triplet-triplet annihilation (TTA) between emitter molecules sensitized via energy transfer from a light harvester moiety. However, the absorption band of proper sensitizers is typically narrow, reducing the fraction of recoverable photons.

Here we demonstrate a method to broaden sTTA-UC absorption by adding a Rhodamine dye to a model bi-component system (PdTPTBP/perylene). This gives rise to a super-sensitized upconversion (ssUC). The dye absorbs light in the transparency window of the sensitizer and transfers to it the harvested energy. ssUC allows a 2-fold increase of the absorbed light, lowering the excitation intensity required to reach the maximum conversion yield to 0.7 suns with an overall enhancement of UC light generation yield of 20%. These results show that ssUC is a general route to design efficient broadband UC systems suitable for SC technology.

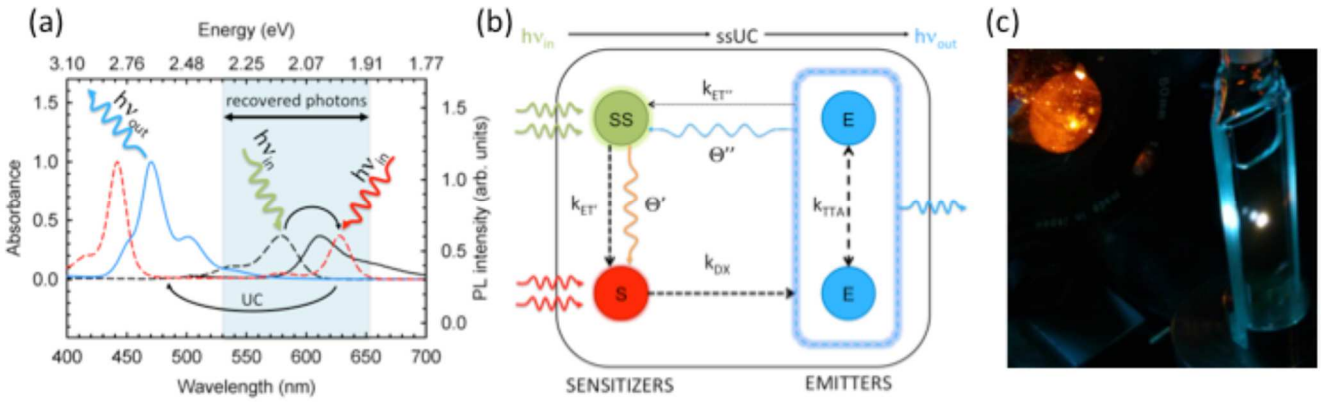

Figure.1 (a) In sTTA-UC systems a sensitizer (red dotted line) absorbs long wavelength light and transfers the energy to an emitter (blue solid line). In ssUC the large spectral gap between sensitizer absorption and emitter PL is filled with a third component, the Super-Sensitizer (absorption: black dotted line; PL: black solid line). The SS absorbs photons in this gap and thanks to the superposition of its PL with the sensitizer absorption transfers the absorbed energy to activate the up-conversion process. (b) Scheme of the ssUC process. The energy absorbed by the SS is transferred to the sensitizer via energy transfer ($k_{ET'}$) and reabsorption of the emitted photons (Θ'). The emitters are excited via Dexter-ET from the sensitizers (k_{DX}) and undergo the TTA process. The SS are re-excited via ET from the singlet-excited emitters ($k_{ET''}$) and via reabsorption of the up-converted emitted photons (Θ''). (c) Image of the ssUC system emitting blue light under red broadband illumination.

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Poster B19

OPTICAL FUNCTIONALIZATION OF SUBSTRATES NANOSTRUCTURED VIA ION BEAM SPUTTERING OR LIGHT INTERFERENCE LITHOGRAPHY

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Here we report on self-organized nanofabrication methods applied to substrates of relevance in the field of optoelectronic and photonics in view of light trapping applications.
In particular we demonstrate that quasi-periodic one-dimensional nanostructures (Fig.1 a,c) formed by Ion Beam Sputtering (IBS) through a self-organised Au stencil mask confer broadband anti-reflective bio-mimetic functionality to crystalline semiconductor substrates (GaAs and Si [1]) as well as to glass and TCO substrates provided their aspect ratio is sufficiently high.
In order to assess the importance of morphological disorder on the broadband optical response we also developed an alternative maskless nano-patterning approach based on large-area Light Interference Lithography (LIL). In this way mono-dispersed arrays of 1-dimensional nanowires (Fig.1 b,d) can be prepared on dielectric and polymeric templates, which can subsequently be employed as highly ordered mono-dispersed stencil masks. Alternatively the ordered templates can be employed as supports for plasmonic nanowire arrays formed via glancing angle metal deposition e.g. in view of nanosensing applications.

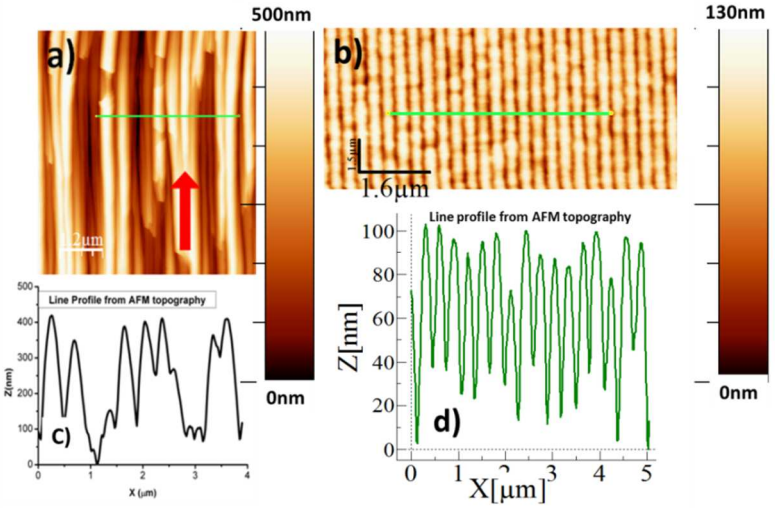

Figure 1: AFM topography (a) and line profile (c) of the nanostructured glass substrate by defocused IBS. Red arrow indicates the in-plane ion-beam direction. AFM topography (b) and line profile (d) of the nanostructured polymeric substrate by Light Interference Lithography.

[1] C. Martella, D. Chiappe, C.Mennucci, F.Buatier de Mongeot, *J. Appl. Phys.* **115** 194308 (2014).

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Poster B20

VAPOR PHASE DOPING AND INFILTRATION OF CONDUCTING POLYMERS

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The aim of this project is to exploit a vacuum based process (atomic layer deposition – ALD) for the top-down synthesis of conducting polymer-inorganic hybrids. Although ALD is commonly seen as a thin film deposition method that results in coatings of substrates with nanoscale films, a modified procedure of the deposition process applied to soft matter results in diffusion of the metal containing precursors into the bulk of the soft substrate[1-3]. Such homogeneous incorporation of metals into polymers without undesired side effects induced by the solvents will enable to alter the physical properties of the hybrid in a way complementary to the common routes such as, composite formation through blending of the polymer with inorganic nanoparticles, etc. The modified ALD process will, dependent on the chemical nature of the metal source (organometallic, metal-organic or halide), allow incorporation of the metal into the polymer and chemical interaction with the backbone and thus an alteration of physical properties. The resulting materials will strongly differ to the commonly synthesized materials as the applied procedure gives access to an entirely new class of hybrid materials, which will be of great impact for emerging applications.
This project is initially focusing on the fundamental understanding of the interactions of the metal-organic precursors with the functional sites of polyaniline (PANI), the impact the interactions have on the conductivity of the material, and finally the possibility to tune the resulting properties by adjusting the parameters for the metal infiltration.
PANI is an organic semiconductor by virtue of its highly conjugated π-delocalized molecular backbone. The application range is very wide and includes electrochromic devices, drug delivery, sensor applications, and rechargeable batteries[4-6]. These applications generally depend upon the switching between the different states of the polymer, namely, leucoemeraldine, emeraldine, and pernigraniline states[5,6], as a response to chemical or electrical trigger. The present work mainly attempts to achieve enhanced doping of PANI (emeraldine) using the aforementioned infiltration method, in order to achieve higher electrical conductivities than with traditional routes. Several metals such as, Titanium or Tin, have been infiltrated into PANI, resulting in good conductivity of the resulting organic-inorganic hybrid polymer.

[1] S. M. Lee, E. Pippel, U. Gösele, C. Dresbach, Y. Qin, C. V. Chandran, T. Bräuniger, G. Hause, M. Knez, *Science* **324** 488 (2009).
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[3] S. M. Lee, E. Pippel, M. Knez. *Chem. Phys. Chem.* **12** 791 (2011).
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Poster B21

GROWTH OF PENTACENE THIN FILMS ON RIPPLED SILICON DIOXIDE SURFACES

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Pentacene ($C_{22}H_{14}$) is a benchmark material for thin film transistor research. The rod-like molecule exhibits several polymorphic crystallographic phases, most notable the thin film phase and Campbell phase achieved in thin films by thermal evaporation on isotropic surfaces. The thin film phase is a surface induced, kinetically favoured phase during growth, while after a critical thickness (depending on substrate temperature and deposition rate) the Campbell phase starts to grow. This growth mechanism is still not fully understood, though strain or an increasing roughness during growth might be crucial parameters. In this work pentacene thin film growth on rippled SiO_2 substrates is studied. Substrates are prepared by low-energy defocused Ar ion beams to obtain wavelike surface structures (ripples). RMS roughness can be tuned from 0.5 nm to 20 nm. Pentacene is deposited by thermal evaporation in ultra-high vacuum with a thickness between a monolayer and 300 nm. Atomic force microscopy is used to characterize the obtained morphologies and polymorphic phases are identified by grazing incidence X-ray diffractometry and X-ray reflectivity. Growth of the thin film phase is dominating even on very rough surfaces but with large mosaicity and decreased critical film thickness causing the Campbell phase to grow earlier. The thin film phase acts as nucleation center for the Campbell phase with molecules oriented in the same direction. On rippled surfaces the molecules align with the underlying structures. Mobility of molecules seems to be increased due to elongation of ripples. On thick samples (1 µm) the high temperature phase is found additional to the Campbell phase and thin film phase.

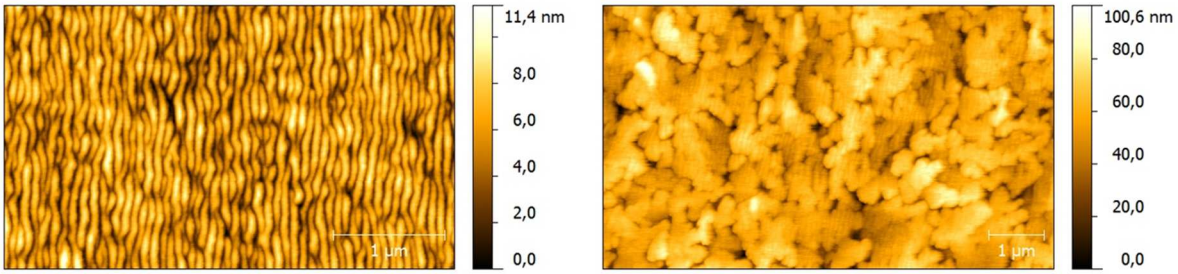

Figure 1: AFM images of a) “rippled” SiO2 substrate after ion beam treatment. RMS roughness 1.7 nm and b) the same substrate after deposition of 300 nm pentacene. The rippled structure is still visible.

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Poster B22

PROTON CONDUCTIVE POLYMERS VIA INITIATED CHEMICAL VAPOR DEPOSITION – SYNTHESIS AND STRUCTURAL CHARACTERIZATION

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Ion-conductive polymer membranes assume a crucial function in various modern-day technologies, ranging from their application in fuel cells to drug delivery or water treatment [1]. Nevertheless, a detailed understanding on the actual proton conduction mechanism is still missing and accessible methods for their synthesis pose a serious challenge. Within this work, proton exchange membranes out of 1H, 1H, 2H, 2H,-perfluorodecyl acrylate (PFDA) and methacrylic acid (MAA) are synthesized via initiated Chemical Vapor Deposition (iCVD). This method allows for the polymerization of various different monomers while ensuring scalability as well as an easy thin film processability [2]. Different processing conditions as well as chemical compositions are studied for these polymer films and their structure, stability and proton conductivity is evaluated. Using X-ray based techniques, the copolymer structure could be elucidated: A bilayer is formed by the perfluorinated pendant chains of PFDA, while the MAA molecules form –COOH enriched regions in between which can then act as ionic channels upon deprotonation of the acid groups [3]. This MMA layer will increase the interplanar distance of the copolymer as observed by a shift of the Bragg reflection in XRR measurements (Figure 1). Within these films, proton conductivities as high as 55 mS/cm are achievable, making them highly comparable to the conductivity of the actual benchmark Nafion® [3].

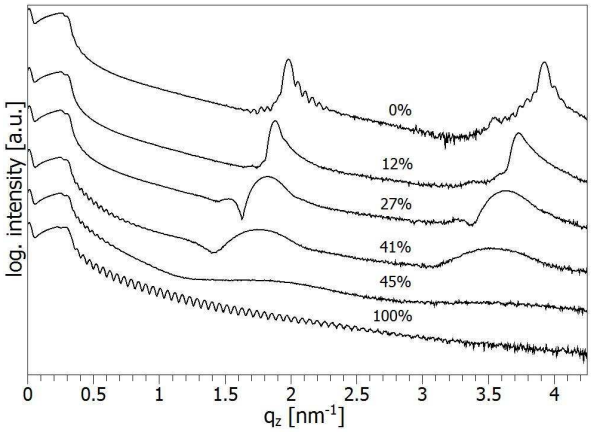

Figure 1. X-ray reflectivity measurements of the polymers with labels indicating the different MAA fraction in the polymer. The films exhibit 1st and 2nd order Bragg peaks from the (001) plane which shift to a lower scattering vector q_z and thus to higher netplane distances for an increasing MAA content.

[1] M. A. Hickner, *Materials Today* **13** (5) 34-41 (2010)
[2] A. M. Coclite, *Surface Innovation* **1** (1), 6-14 (2013)
[3] C. Ranacher, R. Resel, P. Moni, B. Cermenek, V. Hacker, A. M. Coclite, submitted (2015).

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Poster B23

APPEARANCE OF A SURFACE INDUCED CRYSTAL STRUCTURE OF 6,6'-DIBROMOINDIGO

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b. Institute of Pharmaceutical Sciences, University of Graz, Austria
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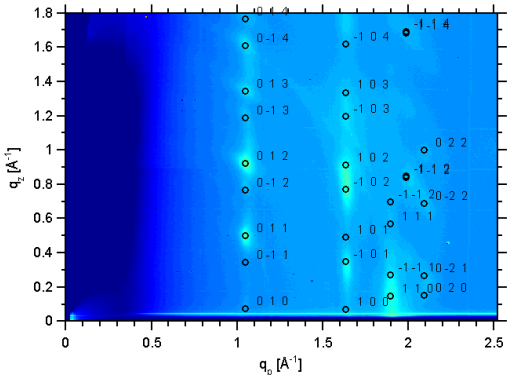
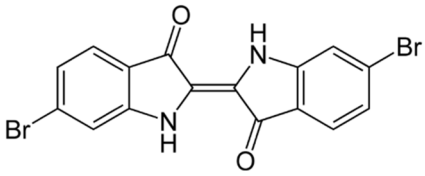
Tyrian Purple (6,6′-dibromoindigo) has been known for many thousand years as a natural dye, but has recently become interesting for its semiconducting properties. Organic semiconductors are a cheap and sustainable way to build electronic devices and therefore of high interest in semiconductor research. Due to the intra- and intermolecular hydrogen bonding Tyrian Purple (TP) shows good charge transport properties and forms highly crystalline films [1]. The crystal bulk phase was solved in 1979 having lattice constants a = 11.50 Å, b = 4.85 Å, c = 12.60 Å and β = 104.0° (space group $P2_1/a$) and two molecules per unit cell [2]. In thin films of TP a surface induced phase is also present [3]. Within this work thin films of TP were prepared by thermal evaporation onto substrates with different surface energies and roughnesses. The substrates were kept at room temperature during evaporation, which is the reason for the appearance of the surface induced crystal phase, whereas at elevated temperatures the bulk phase appears. The film thicknesses were between 2 and 50 nm. Grazing incidence x-ray diffraction (GIXD) experiments were performed at the ESRF, beamline ID10B, using a 2D detector and exposure times between 10 s and 30 s. The reciprocal space maps were analyzed using the softwares xrayutilities[4] and PyGid. They all show similar diffraction patterns which result from a triclinic unit cell with one molecule per cell. The contact plane is 001 and the lattice constant c is in the direction of the long molecular axes of TP, which suggests standing molecules with a small tilt angle with respect to the substrate normal. The lattice constants, especially c, vary a little from sample to sample, but what they all have in common is a prominent peak at q_p = 1.9 $Å^{-1}$ and q_z = 0.2 $Å^{-1}$, which corresponds to the interplanar distance of 3.3 Å between two aromatic rings of TP molecules. This indicates that the crystal structure consists of columns of parallel stacks of aromatic planes, which is significantly different from the bulk phase.



GIXD measurement of a 10 nm film of Tyrian Purple on a plasma etched SiO2 substrate (indexed cell: a=3.85 Å, b=6.02 Å, c=14.94 Å, α=94.35°, β=92.70°, γ=87.05°)



Chemical structure of Tyrian Purple

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[2] P. Süsse, C. Krampe, *Naturwissenschaften* **66** 110 (1979)
[3] A. Pichler, Master Thesis, Techn. Univ. Graz (2013)
[4] D. Kriegner, E. Wintersberger, J. Stangl, *J. Appl. Cryst.* **46** 1162 (2013)

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Poster B24

INFLUENCE OF PMMA CONTAMINATIONS ON ORGANIC SEMICONDUCTOR GROWTH ON CVD GRAPHENE

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Graphene, scalably grown and transferred, is a highly promising material for organic electronics applications. However, controlling the interface properties of graphene with organic semiconductor films remains a key challenge. Here, we investigate the growth characteristics of the organic semiconductor para-hexaphenyl (6P) on chemical vapor deposited graphene that has been transferred with polymethylmethacrylate (PMMA) onto oxidized Si wafers. A major focus is set on the influence of residual PMMA contaminations. These residues are systematically reduced by H2 annealing prior to 6P deposition. Surprisingly, 6P grows in a flat lying needle type fashion irrespective of PMMA contamination and graphene defects [1]. The wrinkles always present on chemical vapor deposited graphene, typically act as preferential nucleation centers. PMMA residuals, however, do limit the length of the resulting 6P needles by restricting molecular diffusion/attachment as is visible in the atomic-force microscopy (AFM) images presented in Figure 1. The implications for organic device fabrication, with particular regard to contamination and defect tolerance are discussed.

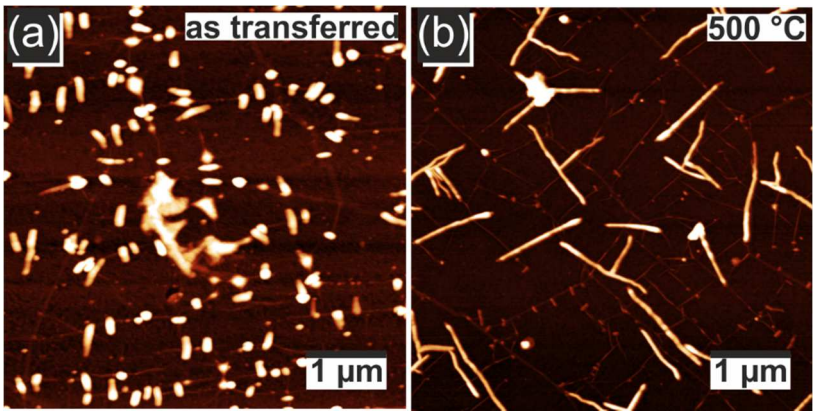

Figure 1. AFM topography images of (a) 6P needles grown on as transferred graphene and (b) graphene annealed in H2 at 500°C prior to deposition. (Height scale: 30 nm; adapted from [1].)

[1] M. Kratzer, et al., *Appl. Phys. Lett.* **106** 103101 (2015).

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Poster B25

INITIAL GROWTH AND DESORPTION STUDIES OF H-BONDED ORGANIC SEMICONDUCTORS ON SiO_2 SUBSTRATES

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Indigo ($C_{16}H_{10}N_2O_2$) and quinacridone ($C_{20}H_{12}N_2O_2$) are part of the group of H-bonded organic dyes with remarkable air stability and attractive semiconducting properties [1]. Understanding the initial growth, namely from the sub-monolayer regime up to a few layers, is a key factor in evaluating possible applications in future microelectronic devices. In this contribution we report on the initial growth, adsorption and desorption behavior of ultra-thin indigo and quinacridone films on a silicon dioxide substrate via physical vapor deposition under UHV conditions. For the investigation of the growth kinetics we used mainly Thermal Desorption Spectroscopy and Auger Electron Spectroscopy, morphology and structure of the films was examined ex-situ by means of Atomic Force Microscopy and X-Ray Diffraction. A major aspect of the research was to elucidate the importance of surface contaminations, in particular carbon, on the film formation. On a sputter cleaned substrate indigo forms a strongly bonded wetting layer which withstands heating to high temperatures. However, with increasing coverage dimers are formed which are less strongly bonded to the substrate and desorb at remarkably low temperature. With further coverage increase a dewetting process starts and islands are formed, in which the molecules are again more strongly bonded [2]. On the C-covered surface, we observe a single monolayer that again subsequently dewets into an island like film. Quinacridone film formation showed similarities to indigo. However, we discovered some unexpected experimental idiosyncracies in this context. It turns out that in the metal Knudsen cell quinacridone partially decomposes and forms a new stable molecule. This will be discussed in more detail in the presentation.

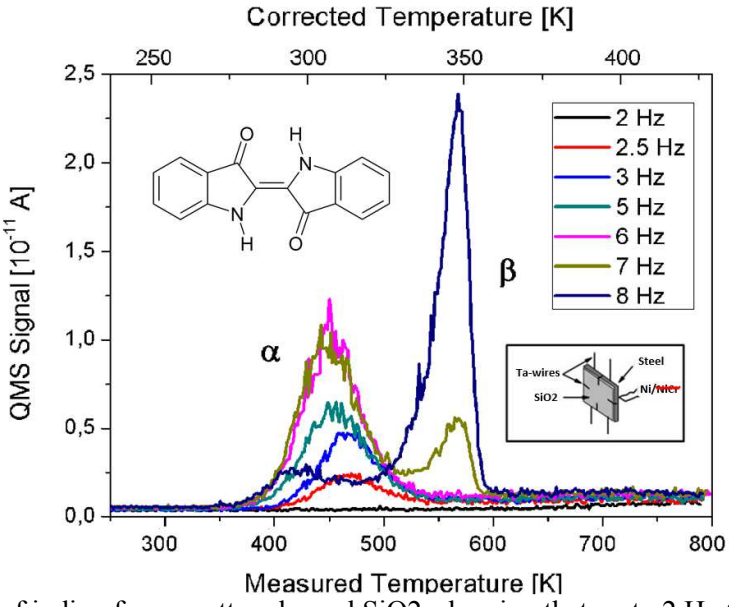

Figure 1. TD spectra of indigo from sputter cleaned SiO2, showing that up to 2 Hz (0.17 nm) no material desorbs, then a weakly bonded wetting layer forms (α-peak), which with increasing coverage dewets by forming islands, in which the molecules are again more strongly bonded (β-peak).

[1] E.D.Glowacki, M. Irimia-Vladu, S. Bauer, N.S. Sariciftci. *J. Mater. Chem. B* **1** 3742 (2013).
[2] B. Scherwitzl, R. Resel, A. Winkler, *J. Chem. Phys.* **140** 184705 (2014)

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Poster B26

INTERDIFFUSION OF FULLERENE DERIVATIVE IN POLY (3,3"' DIDODECYL QUARTER THIOPHENE) THIN LAYER UNDER SOLVENT ANNEALING.

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In order to achieve high photoconversion efficiency of organic solar cells, it is necessary to better understand the diffusion mechanisms in the active layer. The efficiency is highly dependent on the spatial arrangement of the components forming the active layer. Most common used system are layers consisting phases of C60 fullerene derivative and poly (3-alkilo thiophene). These two phases should interpenetrate to increase the interface area (create structure called bulk heterojunction BHJ). The BHJs are usually fabricated by casting from solution of both component in a common solvent. The optimal shape can be also obtained by thermal or vapor solvent annealing of pure component bilayers. In this research the bilayer of of poly (3,3"' didodecyl quarter thiophene) (PQT 12) and [6,6]-Phenyl-C61 butyric acid (2,5-dibromo-3-ethylthiophene) ester was analyzed. The process of interdiffiusion of the fullerene derivative into thin layer of PQT 12 under solvent annealing will be presented. A comprehensive analysis was achieved from the depth profiles collected using the dynamic mode of secondary ion mass spectrometry (dSIMS).

Poster B27

STRUCTURE, MORPHOLOGY AND CHIROPTICAL PROPERTIES OF ANILINO SQUARAINE THIN FILMS

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Organic solar cells (OSC) have been developed to harvest as much light as possible, regardless of its polarization, and to convert the incident sun light efficiently into electricity. Unfortunately, the performance of OSCs is still not competitive with that of inorganic solar cells. However, the benefits of organic material lie more in its structural flexibility, i.e. the possibility to introduce new functionalities upon targeted structural modification of the molecular building block. Small molecular semiconductors, such as squaraines, are advantageous compared to polymeric materials since they allow for a more direct control of the structure at the molecular level and consequently of the solid state properties [1]. Especially the implementation of stereogenic centers allowing for optical activity such as circular dichroism (CD) enables polarization sensitive absorption of light [2]. In this context, the terminal N-substitution pattern of 1,3-bis(N,N-substituted-2,6-dihydroxy-anilino)squaraines is modified with enantiomerically pure functional groups to obtain chiral aggregation of the molecules in spin-casted thin films. Layers additionally blended with a fullerene acceptor should exhibit a distinct circular dichroism, which in turn is expected to result in electrical characteristics of the device that depend on the circular polarization of the incident light.

The current investigations focus on comprehensive optical characterization of neat and blended squaraine thin films, tempered at different temperatures, employing the model squaraine SQIB [3] (see Fig. 1) as well as chiral derivatives. In addition to the optical constants, ellipsometry can also give information about molecular anisotropy and birefringence of the thin films, while X-ray diffraction (XRD) provides information about long range crystallinity and texture. By combining this with microscopic images, the different macroscopic crystalline structures will be isolated and identified such that their molecular orientation will be correlated to the anisotropic optical constants. Spatially and polarization-resolved spectro-microscopy allows for further correlation of morphology and optical properties. In case of the chiral squaraine derivatives the cicular dichroism of aggregates in solution and in thin films is investigated via CD-spectroscopy.

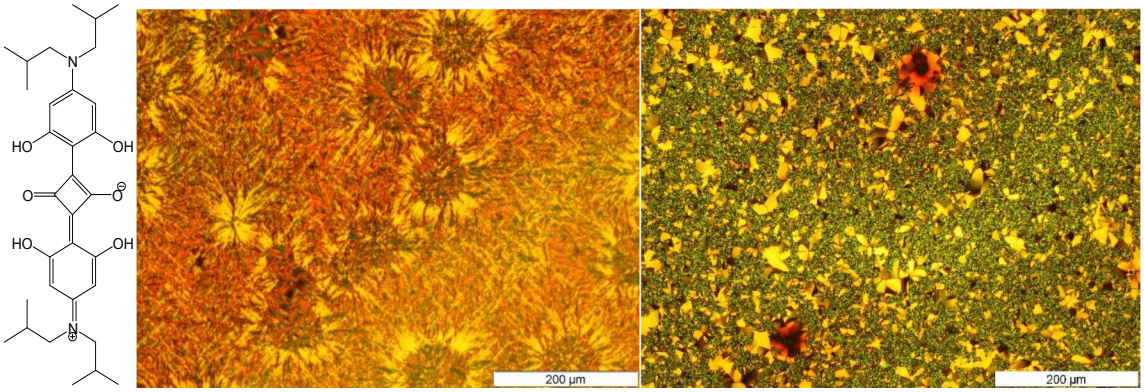

Figure 1. Structural Formula of SQIB (left), microscopy images of a spin coated layers of SQIB, tempered for 2 hours at 60°C (middle) and 120°C (right).

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Poster B28

A FACILE APPROACH FOR THE SYNTHESIS OF RIPPED NANORICE GRAIN SHAPE N DOPED TiO_2 NANOPARTCLES FOR POLLUTANTS PHOTOCATALYTIC DEGRADATION

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Nitrogen-doped TiO_2 nanostructures in the form of nanorice shaped have been prepared by oxidant peroxide method (OPM) at low temperature using stabilized complex of titanium in hydrogen peroxide/ammonia solution as precursors and urea as a source of N dopant. The synthesized material has been characterised using XRD, FE-SEM, HRTEM, XPS, UV-Visible spectroscopy, Ramman spectroscopy and functionally tested using measurements for the photocatalytic degradation of organic dyes (atrazine and RhB) under UV and visible light irradiation. Structural studies carried out by X-ray diffraction analysis shown that undoped TiO_2 crystallizes into the anatase structure as well as at 5 % N-doped introduced a degree of matrix disorder in the latter case. Incorporation of nitrogen into anatase TiO_2 was confirmed due to presence of extended tailing in the absorption edge towards the visible-light range upon nitrogen doping in the optical absorption spectra and also affirmed by FTIR analysis, which indicates successful nitrogen doping. Microscopy studies reveals that the particle size is in the range of 50-70 nm for the undoped TiO_2 and decreased with the increase of N doping as revealed by the variation of particle size graph, nanoparticles are assembled in the form of the nanorice shape with a high surface area (102 m^2g^{-1}). The rate of •OH radical formation on the sample surface under the irradiation of visible light irradiation was executed and found that there is correlation between the formation rate of •OH radicals unit surface area to the order of photocatalytic activity per unit surface area. The N doped TiO_2 nanostructure with nanorice morphology is an efficient photocatalyst for the decomposition of organic dyes under UV light. Pure TiO_2 photocatalyst did not show any significant photocatalytic activity under visible light irradiation as expected; whereas, the 3 at. % N-doped TiO_2 shows excellent activity.

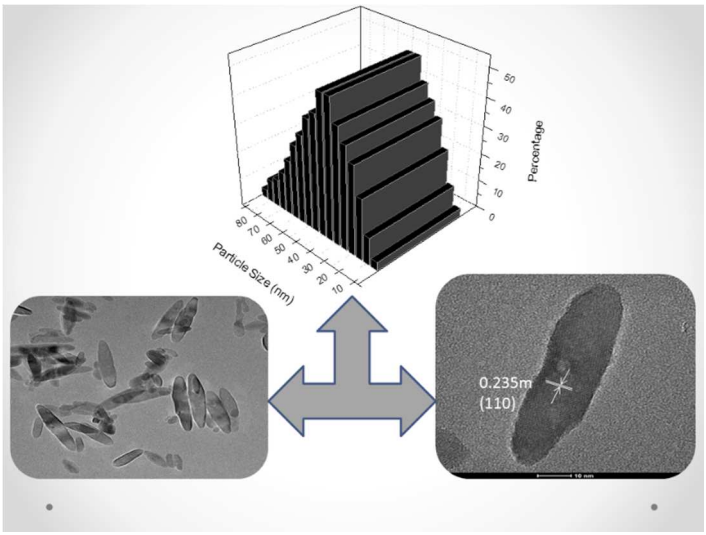

Figure 1 A scheme for representation of morphology and partice size distribution

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Poster B29

A NEW APPROACH FOR STYRENE-BUTADIENE REINFORCEMENT

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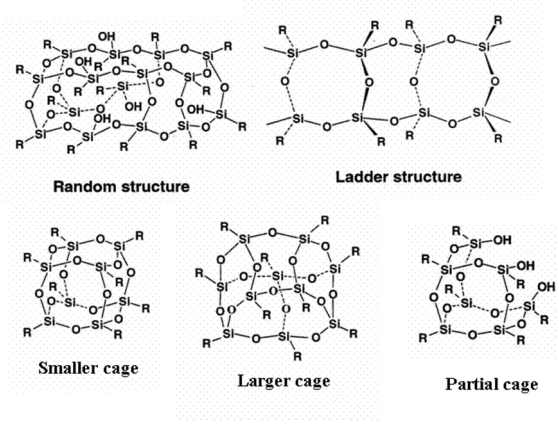
SiO2 is commonly used as nanofiller to enhance the static and dynamic mechanical properties of rubber composites. Tuning the size and shape of the filler nanoparticles along with their surface functionalization allows formation of a homogeneous and continuous percolative network within the rubber matrix, providing effective composite reinforcement. It has been recently demonstrated that particle anisotropy and alignment can provide, beside an increase of the filler-filler interactions, a relevant percentage of immobilized rubber leading to a higher degree of reinforcement [1].
In this context, it has been reported that the incorporation in polymers of polyhedral oligomeric silsesquioxanes (POSS) and ladder-like nanounits (see figure) with tailored morphology, even in small amount, dramatically improves their mechanical properties. These results prompted us to utilize as filler in rubber composites anisotropic nanounits with highly reactive surface groups, allowing to simultaneously tune both filler-filler and filler-rubber interactions. The nanofillers with cage and ladder-like structures functionalized by mercaptopropyl groups have been synthetized by a controlled hydrolysis-condensation reaction [2], and successively introduced in low loadings (0,5%,1%,2% and 4%) in styrene-butadiene polymer (SBR) by swelling (in-situ method).
The filler incorporation has been proved by IR and TGA analysis. The interaction of the filler particles with the polymeric chains has been evaluated with TD-NMR spectroscopy and with electron spin resonance (ESR) by monitoring the behavior of nitroxide radicals introduced as a spin-probe in the composites. Preliminary dynamic mechanical measurements on both uncured and vulcanized nanocomposites indicated that their introduction in very small amount provide an effective reinforcement of SBR matrix.
The overall results indicate that the adopted approach is promising for effectively improving the mechanical properties and for a potential reduction of silica utilization in rubber compounding.



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Poster B30

INFLUENCE OF TiO_2(110) SURFACE ROUGHNESS ON GROWTH AND STABILITY OF THIN ORGANIC FILMS

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We have investigated growth and stability of molecular ultra-thin films on ion beam modified TiO_2(110) surfaces. The surface morphology of developed *para*-hexaphenyl (6P) structures was examined with AFM, tapping and contact mode, and SEM techniques. The TiO_2(110) surface was modified with low energy, 2 keV, noble gas (Ar, Kr, Xe) ion beam irradiating the surface at oblique, 75 degree off normal, incidence. Under the experimental conditions used, the ion bombardment of titanium dioxide surface resulted in nanoripple pattern formation. We have found that the ripples period, height and length are fluence, projectile and temperature dependent. The 6P sub-monolayer deposition was carried in UHV by process of molecular MBE, performed at room temperature. The deposition process was performed on two kind of substrate surfaces: on freshly prepared ion beam-modified TiO_2(110) and on identically prepared pre-patterned surfaces air passivated prior to deposition.

It has been found, that the 6P deposition on rippled substrate both, fresh and air-passivated, results in formation of anisotropic islands composed of upright-standing molecules [1]. In the case of shallow rippled surface (surface height variation lower than the length of 6P molecules of 2.7 nm) the islands are stable and can be imaged by AFM and SEM. On the other hand, for deeper ripples (surface height variation in the range of 10 nm) the created 6P islands are not stable against the interaction with AFM tip and can be imaged only with SEM. We have found that the local curvature of substrate structure influences the bonding between the nearest standing molecules in the island. Higher local slope angles result in larger shift between the nearest standing molecules along their length. It induces weaker bond between them and, finally, leads to less stable island.

For the case of the stable islands, we have also found that the islands can be moved with the AFM tip in contact mode. However, the strength of the substrate-island interaction depends on the TiO_2(110) surface conditions. For the case of manipulation of the islands grown on freshly prepared ripples, higher load has to be applied compared to the case of the islands grown on air-passivated ripples. We will show how the substrate surface anisotropy and AFM scanning conditions influence the possibility of the islands movement.

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